



Copper(II)-coordinated organic nanotube: A novel heterogeneous catalyst for various oxidation reactions

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ABSTRACT

Copper(II)-coordinated organic nanotube can function as a heterogeneous catalyst for oxidation of a variety of organic compounds in the presence of hydrogen peroxide and *tert*-butyl hydroperoxide. The morphology of this catalyst remained same before and after the oxidation reactions. The catalyst can be reused for several times. In the presence of hydrogen peroxide, Copper(II)-coordinated organic nanotube formed a stable brown color peroxo bridge intermediate. But such intermediate did not form with *tert*-butyl hydroperoxide.

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1. Introduction

A large number of catalytic oxidation processes [1–13] based upon the combination of metal salts and atom-efficient oxidants, such as molecular oxygen [14] or H₂O₂ [15] or *tert*-butyl hydrogen peroxide (TBHP) [16], have been recently developed. Among them, heterogeneous oxidation catalysts draw much attention due to their separability and reusability. Copper is the common metal for studies of oxidation catalysts. There are various reports of copper containing porous and nonporous heterogeneous catalysts, which were active for selective oxidations of a variety of organic compounds in the presence of atom-efficient oxidants [17–24]. But none of the reported copper containing heterogeneous catalysts has been shown to oxidize a wide variety of organic substrates with oxidants alone. Heterogeneous catalysts sometime required high energy processes for their preparation. The presence of scaffold in the heterogeneous catalysts, such as silica, titania and zeolite, is another problem. We have reported tubular molecular assemblies with well-defined dimensions (organic nanotubes) from various types of amphiphiles [25–28]. These amphiphiles can be produced from low cost natural materials through several steps under mild conditions. The nanotubes have large surface area on the inner and outer wall. It occurred to us that the nanotubes would be novel support for the metal catalysts. Indeed, the nanotubes consisting of peptide-lipid (C-terminated) can form coordination complexes with metal ions [29], which should have the catalytic activities.

Here we report the Copper (II)-coordinated organic nanotube (abbreviated as Cu-ONT complex **1** hereafter) as a catalyst for oxidation of wide ranges of organic compounds in presence of oxidants, H₂O₂ or TBHP. This catalyst did not show any catalytic activity with molecular oxygen. We also report here the synthesis of stable peroxo bridge nano-intermediate in dry state. The Cu-ONT complex **1** decomposed the hydrogen peroxide to corresponding water and oxygen, analogous to catalase enzyme via formation of peroxo bridge nano-intermediate [30].

2. Experimental Section

2.1. Materials

All the test substrates and aqueous solutions of 30% H₂O₂ and 70% TBHP were purchased from Wako Chemical Company and used as received.

2.2. Instrumental Details

Elemental analyses were performed on a Perkin–Elmer 2400 CHNS Elemental Analyzer II. Fourier transformation infrared (FTIR) spectra were recorded on a Jasco FT/IR-620 spectrometer with ATR unit. Thermogravimetric and differential thermal analyses (TG/DTA) were carried out with a Seiko TG-DTA 6200-S under atmospheric condition. These measurements were performed with a temperature ramp of 4 °C / min between 30 °C and 530 °C. Diffuse reflectance (DR)–UV–Vis spectra were recorded on a Shimadzu UV-3150 UV-VIS-NIR spectrophotometer. X-band EPR spectra of all the complexes were recorded on a JEOL JES-RE Series EPR spectrometer at room temperature. X-ray

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powder diffraction (XRPD) was performed on a Rigaku R-AXIS IV X-ray diffractometer monochromated Cu-K α radiation (40.0 kV, 30.0 mA) at room temperature. Field Emission Scanning Electron Microscope (FE-SEM) measurement was carried out with Hitachi S-4800 field-emission microscope. The reaction solution was analyzed by GC (FID, SE-30 glass column and DBWAX capillary column (0.25 mm i. d., 30 m) and assignments were made by comparison with authentic samples analyzed under the same conditions.

2.3. Preparation of the Cu-ONT complex 1

The Cu-ONT complex **1** was prepared as follows: Aqueous solution (5 ml) of copper nitrate (1 g) and aqueous solution (5 ml) of sodium salt of glycylglycine lipid, 2-(2-(2-tetradecanamidoacetamido) acetamido) acetic acid (2 g) were mixed at room temperature and stand for 1 h. Then the suspension was filtered and was washed with large excess of water. The greenish blue color precipitate was collected and dried under vacuum at room temperature. Elemental analysis: found: C 53.34, H 9.02, N 6.84%. calcd for: Cu C₃₆ H₆₆ N₄ O₈2H₂O: C 52.82, H 9.11, N 6.85%. FTIR: 1640, 1550 and 1028 cm⁻¹. DR-UV spectrum: λ_{\max} = 255 and 750 nm. EPR: Active.

2.4. Preparation of the Cu-ONT complex 3

The peroxy bridge complex was prepared as follows: 30% H₂O₂ (1.02 g, 30 mmol) was added to a suspension of the Cu-ONT complex **1** (0.409 g, 1 mmol) in acetonitrile (5 ml) at room temperature. The

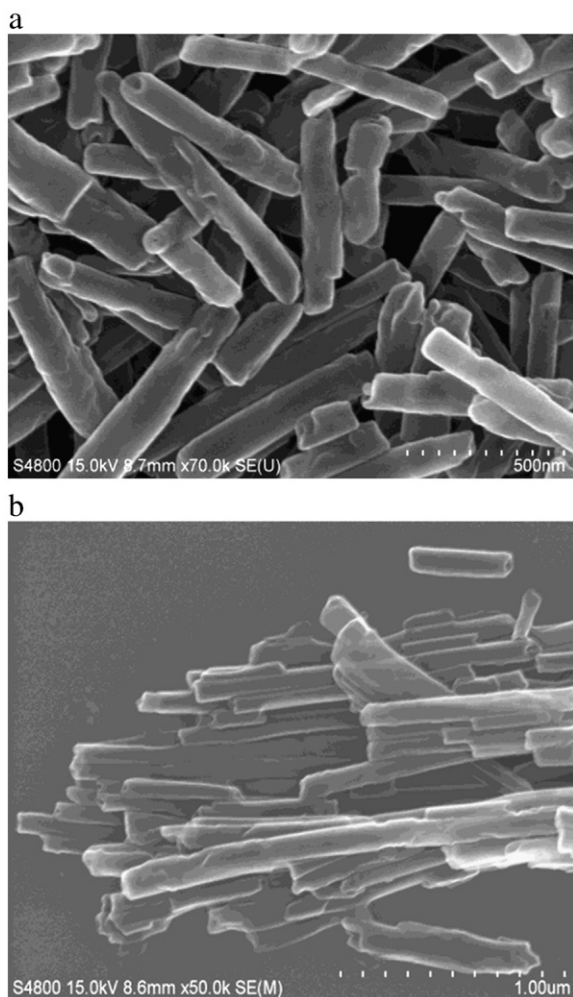


Fig. 1. FE-SEM images: (a) the Cu-ONT complex **1** and (b) the Cu-ONT complex **4**.

Table 1
Oxidation of alcohols with H₂O₂ and TBHP catalyzed by the Cu-ONT complex **1**.

Substrate	Product	Conversion (%) ^c		Selectivity (%) ^c		TON ^d	
		H ₂ O ₂ ^a	TBHP ^b	H ₂ O ₂	TBHP	H ₂ O ₂	TBHP
Benzyl alcohol	Benzaldehyde	25	50	81	75	20.25	37.50
1-Phenylethanol	Acetophenone	3	20	>99	>99	2.97	19.8
Cyclohexanol	Cyclohexanone	14	22	>99	>99	13.86	21.78
Cyclododecanol	Cyclododecanone	10	25	>99	>99	9.9	24.75
1-Octanol	1-Octanal	20	37	78	71	15.6	28.86
2-Octanol	2-Octanone	17	29	>99	>99	16.83	28.71

^a Cu-ONT complex **1** (0.01 mmol), alcohols (1 mmol), 30% H₂O₂ (15 mmol), and CH₃CN (5 ml), were stirred at 60 °C for 5 h in air.

^b Cu-ONT complex **1** (0.01 mmol), alcohols (1 mmol), 70% TBHP (2 mmol), and CH₃CN (5 ml), were stirred at 60 °C for 5 h in air.

^c Determined by GC analysis on the basis of substrates charged with biphenyl as internal standard.

^d TON = mol of product / mol of catalyst.

color of the reaction suspension changed from greenish blue to green within 15 minutes after addition of H₂O₂. The green-colored reaction suspension changed into brown color within 3 h stirring. This brown color precipitate was collected after 12 h and was washed with acetonitrile and water. The precipitate was dried under vacuum at room temperature. Elemental analysis: found: C 53.17, H 8.47, N 6.83%. calcd for: Cu C₃₆ H₆₈ N₄ O₈2H₂O: C 52.95, H 8.81, N 6.85%. FTIR : 1725, 1655 1640, 1550 and 1028 cm⁻¹. DR-UV spectrum: λ_{\max} = 255, 407, 475 and 725 nm. EPR: Silent.

2.5. Catalytic oxidation of organic compounds

The Cu-ONT complex **1** (0.01 mmol) was suspended in the solution of substrates (1 mmol) in CH₃CN (5 ml). Then the mixture was allowed to equilibrate at a reaction temperature of 60 °C. We added different amount of H₂O₂ or TBHP (as illustrated in foot note of each table) in the mixture with stirring. The stirring was continued for five hours at 60 °C in open atmosphere. The conversion and selectivity were determined by GC analysis on the basis of substrates charged with biphenyl as internal standard.

In every reuse studies, the solid Cu-ONT complex **1** was washed with excess acetonitrile to remove the organic compounds present in the cavities of the catalyst before the samplings. Then the Cu-ONT complex **1** was washed with water several times and dried under vacuum.

Table 2
Oxidation of α , β -unsaturated alcohols and aldehydes with H₂O₂ and TBHP catalyzed by Cu-ONT complex **1**.

Substrate	Product	Conversion (%) ^c		Selectivity (%) ^c		TON ^f	
		H ₂ O ₂	TBHP	H ₂ O ₂	TBHP	H ₂ O ₂	TBHP
Cinnamyl alcohol	Cinnamaldehyde	17 ^a	33 ^b	87	91	14.79	30.03
<i>trans</i> -Hex-2-ene-1-ol	<i>trans</i> -Hex-2-ene-1-al	27 ^a	46 ^b	99	99	26.73	45.54
Cinnamaldehyde	Cinnamic acid	16 ^c	23 ^d	67	75	10.72	17.25
<i>trans</i> -Hex-2-ene-1-al	<i>trans</i> -Hex-2-ene-1-oic acid	10 ^c	25 ^d	99	99	9.9	24.75

^a Cu-ONT complex **1** (0.01 mmol), substrate (1 mmol), 10% H₂O₂ (2 mmol), 5 ml CH₃CN, stirring 5 h at 60 °C.

^b Cu-ONT complex **1** (0.01 mmol), substrate (1 mmol), 10% TBHP(2 mmol), 5 ml CH₃CN, stirring 5 h at 60 °C.

^c Cu-ONT complex **1** (0.01 mmol), substrate (1 mmol), 30% H₂O₂ (3 mmol), 5 ml CH₃CN, stirring 5 h at 60 °C.

^d Cu-ONT complex **1** (0.01 mmol), substrate (1 mmol), 30% TBHP(3 mmol), 5 ml CH₃CN, stirring 5 h at 60 °C.

^e Determined by GC analysis on the basis of substrates charged with biphenyl as internal standard.

^f TON = mol of product / mol of catalyst.

Table 3
Oxidation of TMP with H₂O₂ and TBHP catalyzed by the Cu-ONT complex **1**.

	H ₂ O ₂ ^a	TBHP ^b
Conversion (%) ^c	trace ^d	52
Selectivity (%) ^c	trace ^d	93
^e TON	48.36	

^a Cu-ONT complex **1** (0.01 mmol), substrate (1 mmol), 30% H₂O₂ (15 mmol), 5 ml CH₃CN, stirring 5 h at 65 °C.

^b Cu-ONT complex **1** (0.01 mmol), substrate (1 mmol), 70% TBHP (2 mmol), 5 ml CH₃CN, stirring 5 h at 65 °C.

^c Determined by GC analysis on the basis of substrate charged with biphenyl as internal standard.

^d trace (<1%).

^e TON = mol of product / mol of catalyst.

3. Results and Discussion

3.1. Characterization of the Cu-ONT complex **3**

Before the oxidation studies, we tested the stability of the Cu-ONT complex **1** with varying amounts of 30% H₂O₂ and 70% TBHP (10–100 folds excess of Cu-ONT complex **1**) in acetonitrile medium. The Cu-ONT complex **1** did not leach into the solution after 24 h stirring, since we did not observe any absorption bands corresponding to copper ion in UV-Vis spectra (see Supporting Information). But we found a very interesting two stage color changes upon addition of H₂O₂. When the greenish blue color Cu-ONT complex **1** was stirred in the presence of H₂O₂, first it changed to green color compound (Cu-ONT complex **2**) within 15 minutes. Then it changed completely to brown color compound (Cu-ONT complex **3**) within 3 h. During its existence in reaction medium, lots of bubble formed. After 24 h, bubbling ceased and brown color Cu-ONT complex **3** changed to greenish blue color of compound (Cu-ONT complex **4**) which was exactly same color of the Cu-ONT complex **1** (see Supporting Information). However, we did not observe any color change with TBHP. The investigation is going on in our laboratory to understand the reason. To understand the inherent mechanism during the color changes, we isolated all complexes and then characterized those by FTIR, elemental analysis, TG/DTA, DR-UV-Vis, EPR, XRPD and FE-SEM.

FTIR spectra of the Cu-ONT complexes **2** and **4** were very similar to the Cu-ONT complex **1**. The bands appeared at 1640 and 1550 cm⁻¹ due to amide I (mainly ascribed to the C = O stretching band) and II bands (mainly the N-H deformation band). But in case of the Cu-ONT complex **3**, two new bands which correspond to non-chelating carboxylic acid group appeared at 1655 and 1725 cm⁻¹ along with amide bands (see Supporting Information). The elemental analysis result of the Cu-ONT complex **3** was very similar to its probable composition. But for the Cu-ONT complex **2**, we could not find out its exact composition. The elemental analysis data of complex **4** was same to the Cu-ONT

Table 4
Oxidation of alkane and alkyl benzene with TBHP catalyzed by the Cu-ONT complex **1**.

Substrate	Product	Conversion (%) ^c		Selectivity (%) ^c		TON ^e	
		H ₂ O ₂	TBHP	H ₂ O ₂	TBHP	H ₂ O ₂	TBHP
Cyclohexane	Cyclohexanone	30 ^a	70 ^b	51	70	15.3	49
	Cyclohexanol			49	30	14.7	21
Ethyl benzene	Acetophenone	trace ^d	25 ^b	-	82	-	20.5
Diphenylmethane	Benzophenone	trace ^d	43 ^b	-	99	-	42.57
Tetraline	α-Tetralone	trace ^d	32 ^b	-	99	-	31.68

^a Cu-ONT complex **1** (0.01 mmol), substrate (1 mmol), 30% H₂O₂ (15 mmol), 5 ml CH₃CN, stirring 5 h at 60 °C.

^b Cu-ONT complex **1** (0.01 mmol), substrate (1 mmol), 70% TBHP (2 mmol), 5 ml CH₃CN, stirring 5 h at 60 °C.

^c Determined by GC analysis on the basis of substrates charged with biphenyl as internal standard.

^d trace (<1%).

^e TON = mol of product / mol of catalyst.

Table 5
Epoxidation of alkenes and terpene with H₂O₂ and TBHP catalyzed by Cu-ONT complex **1**.

Substrate	Product	Conversion (%) ^c		Selectivity (%) ^c		TON ^d	
		H ₂ O ₂ ^a	TBHP ^b	H ₂ O ₂	TBHP	H ₂ O ₂	TBHP
Cyclohexene	Cyclohexene Oxide	21	41	78	81	16.38	63.18
Styrene	Styrene Oxide	18	31	77	80	13.86	24.8
α-Pinene	α-Pinene oxide	15	26	83	85	12.45	22.1

^a Cu-ONT complex **1** (0.01 mmol), substrate (1 mmol), 30% H₂O₂ (15 mmol), 5 ml CH₃CN, stirring 2 h at 60 °C.

^b Cu-ONT complex **1** (0.01 mmol), substrate (1 mmol), 70% TBHP (2 mmol), 5 ml CH₃CN, stirring 2 h at 60 °C.

^c Determined by GC analysis on the basis of substrates charged with biphenyl as internal standard.

^d TON = mol of product / mol of catalyst.

complex **1**. The TG/DTA measurements of Cu-ONT complexes **1**, **2** and **4** initially showed very similar weight loss of 4.54% between 80–110 °C, which corresponded to removal of two water molecules. The Cu-ONT complex **3** showed weight loss of 3.8% between 110–140 °C (see Supporting Information), which similar to the decomposition of peroxy group literary reported [24]. The DR-UV-Vis spectrum of the Cu-ONT complex **1** showed two absorption bands at 259 and 725 nm due to the amide group present in ONT and d-d transition. The spectrum of Cu-ONT complex **4** was identical to Cu-ONT complex **1**. In the Cu-ONT complex **3**, a new broad ligand-to-metal charge transfer (LMCT) band with two small humps appeared at 407 and 475 nm along with the amide band at 255 nm. This LMCT band revealed coordination of peroxy ligand to dicopper sites [24]. The DR-UV-Vis spectrum of the Cu-ONT complex **2** showed same amide and LMCT bands like the Cu-ONT complex **1** but a new LMCT band emerged at 475 nm (see Supporting Information). The XRPD measurement of the final compound, i. e., Cu-ONT complex **4** was similar to the Cu-ONT complex **1** (see Supporting Information). Cu-ONT complex **3** was EPR silent states due to anti-ferromagnetic coupling between two copper (II) atoms [24]. FE-SEM measurements showed that the Cu-ONT complex **4** had nanotube morphology same as the Cu-ONT complex **1** (Fig. 1).

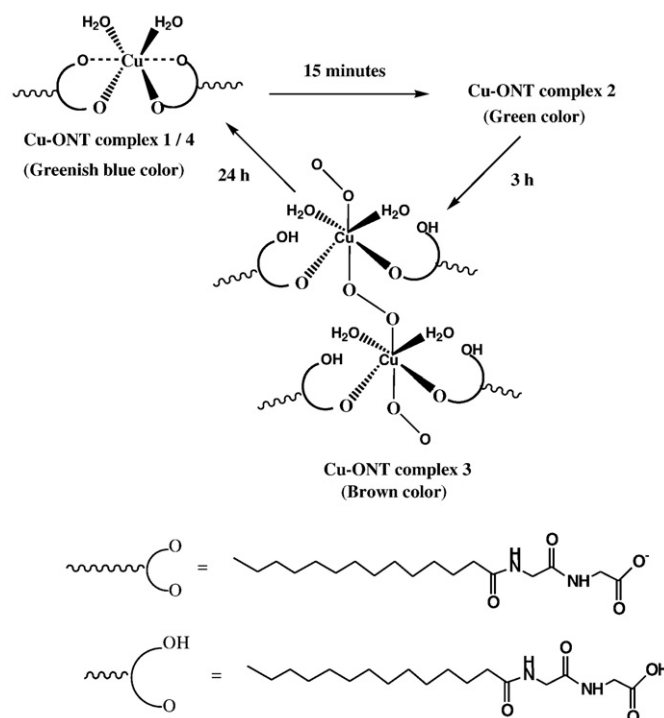
**Scheme 1.** Probable mechanism for formation of different color complexes.

Table 6
Reuse of Cu-ONT complex **1** with H₂O₂ and TBHP for 2-octanol oxidation.

	H ₂ O ₂ ^a				TBHP ^b			
Reused number	1	2	3	4	1	2	3	4
Conversion (%) ^c	17	19	18	16	29	28	26	26

^a Complex **1** (0.01 mmol), 2-Octanol (1 mmol), 30% H₂O₂ (15 mmol), and CH₃CN (5 ml), were stirred at 60 °C for 5 h in air.

^b Complex **1** (0.01 mmol), alcohols (1 mmol), 70% TBHP (2 mmol), and CH₃CN (5 ml), were stirred at 60 °C for 5 h in air.

^c Determined by GC analysis on the basis of substrates charged with biphenyl as internal standard.

All the results suggested that the Cu-ONT complex **1** reacted with H₂O₂ and formed the brown color Cu-ONT complex **3** which was peroxy complex. Although the Cu-ONT complex **3** was stable in dry state, it slowly decomposed in solution with bubbling and regenerated Cu-ONT complex **1**. The bubbling may be molecular oxygen, displaced from Cu-ONT complex **3**. Possibly, the Cu-ONT complex **2** was a reactive intermediate. But at this moment, it is difficult to analyze the exact composition. Heat treatment accelerated the cycle of color changes from 24 h to 6 h.

3.2. Catalytic oxidation

We investigated catalytic activity of Cu-ONT complex **1** for oxidation of a wide range of organic substrates such as alcohols, α , β -unsaturated alcohols and aldehydes, phenol, alkane, alkyl benzenes, alkenes and terpene. The details are described below.

3.2.1. Alcohol oxidation

Cu-ONT complex **1** can act as a selective oxidation catalyst for various primary and secondary alcohols to corresponding aldehydes and ketones (see Table 1). When we used 15 folds excess of 30% H₂O₂ and two folds excess of 70% TBHP compared to substrates, we got best conversion. The conversions of primary and secondary alcohols were ranging from 20–50% with TBHP while 3–25% with H₂O₂ with good selectivity.

3.2.2. α , β -unsaturated alcohols and aldehydes oxidation

We took some α , β -unsaturated alcohols and aldehydes as substrates for oxidation and got corresponding aldehydes and carboxylic acids without byproducts such as epoxide. Selective oxidation of cinnamyl alcohol to aldehyde needed two folds excess of 10% H₂O₂ or TBHP compared to substrates. Higher concentration of H₂O₂ or TBHP produced many byproducts. In contrast, oxidation of cinnamaldehyde required three folds excess of 30% H₂O₂ or TBHP. We found same tendency on stepwise oxidation of *trans*-hex-2-ene-1-ol to corresponding carboxylic acid. Table 2 clearly shows that the Cu-ONT complex **1** can control the oxidation reactions depending on the concentration of oxidants.

Table 7
Reuse of Cu-ONT complex **1** with H₂O₂ and TBHP for cinnamyl alcohol oxidation.

	H ₂ O ₂ ^a				TBHP ^b			
Reused number	1	2	3	4	1	2	3	4
Conversion (%) ^c	17	16	17	15	33	32	32	33
Selectivity (%) ^c	87	86	87	85	91	92	90	91

^a Cu-ONT complex **1** (0.01 mmol), substrate (1 mmol), 10% H₂O₂ (2 mmol), 5 ml CH₃CN, stirring 5 h at 60 °C.

^b Cu-ONT complex **1** (0.01 mmol), substrate (1 mmol), 10% TBHP (2 mmol), 5 ml CH₃CN, stirring 5 h at 60 °C.

^c Determined by GC analysis on the basis of substrates charged with biphenyl as internal standard.

Table 8
Reuse of Cu-ONT complex **1** with TBHP for TMP oxidation.

	TBHP ^a			
Reused number	1	2	3	4
^b Conversion (%)	52	50	49	51
^b Selectivity (%)	93	91	93	92

^a Complex **1** (0.01 mmol), substrate (1 mmol), 70% TBHP (2 mmol), 5 ml CH₃CN, stirring 5 h at 65 °C.

^b Determined by GC analysis on the basis of substrates charged with biphenyl as internal standard.

3.2.3. Phenol oxidation

For phenol oxidation, we used 2, 3, 6-trimethyl phenol (TMP) as a test substrate. It would be oxidized to trimethyl-1, 4-benzoquinone (TMQ) which is a key intermediate for production of vitamin E. We observed best conversion of TMP (52%) when we used two folds excess of 70% TBHP compared to substrates (see Table 3). But we did not observe any oxidation with H₂O₂.

3.2.4. Alkane and alkyl benzene oxidation

We got 30% and 70% conversion of cyclohexane when we used 15 folds excess of 30% H₂O₂ and two folds excess of 70% TBHP respectively (see Table 4). We got 25–32% conversion of the alkyl benzenes with two folds excess of 70% TBHP. But we observed almost no oxidation result with H₂O₂ (see Table 4).

3.2.5. Alkenes and terpene epoxidation

Here, we took cyclohexene, styrene and α -pinene as test substrates. We got 15–21% conversion of the substrates to corresponding epoxide with 15 folds excess of 30% H₂O₂ while 26–41% conversion with two folds excess of 70% TBHP (see Table 5).

According to the results, oxidation by TBHP provided higher conversion than H₂O₂. This difference was due to decomposition of H₂O₂ [31] via formation of Cu-ONT complex **3** (see Scheme 1). This side reaction competed with the substrates oxidation on Cu-ONT complex **1** and reduced the oxidation product.

3.2.6. Reuse property of the Cu-ONT complex **1**

Cu-ONT complex **1** was easily reused in the oxidation of 2-octanol, cinnamyl alcohol, TMP, cyclohexane and styrene (see Tables 6–10). For all cases, conversion and selectivity of the catalytic reactions were not significantly different through first to fourth use of the Cu-ONT complex **1**.

4. Conclusions

In conclusion, Cu-ONT complex **1** can function as a heterogeneous oxidation catalyst with H₂O₂ and TBHP. The large surface area of nanotube made Cu-ONT complex **1** a good catalyst. Due to its operational simplicity, generality and efficacy, this material is applicable to the oxidation of a variety of organic compounds. It is

Table 9
Reuse of Cu-ONT complex **1** with H₂O₂ and TBHP for cyclohexane oxidation.

	H ₂ O ₂ ^a				TBHP ^b			
Reused number	1	2	3	4	1	2	3	4
Conversion (%) ^c	30	28	31	31	70	70	68	71
Selectivity (%) ^c								
Cyclohexanone	53	51	52	53	71	70	72	71
Cyclohexanol	47	49	48	47	29	30	28	29

^a Complex **1** (0.01 mmol), substrate (1 mmol), 30% H₂O₂ (15 mmol), 5 ml CH₃CN, stirring 5 h at 60 °C.

^b Complex **1** (0.01 mmol), substrate (1 mmol), 70% TBHP (2 mmol), 5 ml CH₃CN, stirring 5 h at 60 °C.

^c Determined by GC analysis on the basis of substrates charged with biphenyl as internal standard.

Table 10
Reuse of Cu-ONT complex **1** with H₂O₂ and TBHP for styrene epoxidation.

	H ₂ O ₂ ^a				TBHP ^b			
Reused number	1	2	3	4	1	2	3	4
^c Conversion (%)	18	21	19	20	31	30	33	31
^c Selectivity (%)	77	77	78	78	80	78	77	81

^a Cu-ONT complex **1** (0.01 mmol), substrate (1 mmol), 30% H₂O₂ (15 mmol), 5 ml CH₃CN, stirring 2 h at 60 °C.

^b Cu-ONT complex **1** (0.01 mmol), substrate (1 mmol), 70% TBHP (2 mmol), 5 ml CH₃CN, stirring 2 h at 60 °C.

^c Determined by GC analysis on the basis of substrates charged with biphenyl as internal standard.

important to mention that the morphology of Cu-ONT complex **1** does not change after oxidation reaction which is the key factor for its reusable property. Interestingly, we have made a very stable brown color peroxy bridge nano-intermediate (Cu-ONT complex **3**) in solid state at room temperature. Formation of Cu-ONT complex **3** diminishes the oxidation reactions. But it is still good to control some oxidations. The application of Cu-ONT complex **3** is going on in our laboratory now.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2010.07.013.

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