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# Reactivity of Copper Nanopowders in a Model Reaction of Isopropylbenzene Oxidation

## T. S. Skorokhodova, N. S. Kobotaeva, and E. E. Sirotkina

Institute of Petrochemistry, Siberian Division, Russian Academy of Sciences, Tomsk, Russia

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Abstract—The reactivity of copper nanopowders produced by an electric explosion of a conductor or mechanochemically was studied. Oxidation of isopropylbenzene was used as a model reaction. The dependence of the oxygen uptake rate on the specific surface area of a copper nanopowder and on the method used for its production is discussed. A possible mechanism of isopropylbenzene oxidation in the presence of copper nanopowders is suggested.

The intermediate position occupied by nanoparticles in passing from a bulk metal to a separate atom predetermines the deviation of their physicochemical properties from those of bulk metals, on the one hand, and from the properties of isolated atoms, on the other. This deviation is manifested in electronic, magnetic, optical, and other properties of nanoparticles with a characteristic size of several tens of nanometers to several nanometers [1]. Numerous summarizing papers concerning methods for preparation and stabilization of nanoparticles and their optical and other properties have already appeared, whereas studies of chemical transformations involving nanoparticles are only in their initial stage [2].

It is known [3] that nanosize powders (NPs) of metals show an increased reactivity, compared to compact metals. For example, reactions that do not occur in the presence of some metals or require severe conditions readily proceed in the presence of metal nanopowders. In particular, synthesis of complex compounds (phthalocyanines and tetraphenylporphyrins) with the use of copper and indium NP [4, 5] is performed under milder conditions (room temperature and atmospheric pressure) than the conventional synthesis with metal salts. Use of metal NPs as catalysts for oxidation of organic compounds is known. It was shown in [6] that the uptake of oxygen in oxidation of isopropylbenzene (IPB) in the presence of NPs of copper and cobalt proceeds at a sufficiently high rate even at 30°C without any initiator.

In this study we examined the reactivity of copper NP, obtained by an electric explosion of a conductor (EEC) or mechanochemically, in a model reaction of IPB oxidation.

#### EXPERIMENTAL

As objects of study served copper NP obtained by an electric explosion of a conductor in the atmosphere of nitrogen, argon, and xenon, as well as copper NP produced mechanochemically on an AGO-2 installation in the presence of organic and inorganic additives.<sup>1</sup> The additives were used to raise the specific surface area of the mechanochemically produced NP [7]. Copper nanopowders were produced by mechanical treatment (MT) in AGO-2 planetary-centrifugal high-energy-intensity mills in the presence of an organic surfactant (2,2,3,3,4,4,5,5-octafluorovaleramide) in an amount of 10% for 10 (Cu I), 20 (Cu II), and 30 min (Cu III). Copper powders were also prepared by mechanical treatment in the presence of 15 wt % CuCl<sub>2</sub> (CuCl<sub>2</sub> was washed out with ethanol after MT) on an AGO-2 installation for 10 (Cu 1), 20 (Cu 2), and 30 min (Cu 3). The physicochemical parameters and the preparation conditions of copper NPs used in this study are listed in Table 1.

IPB was oxidized on a gasometric installation [8]. A 0.7-M portion of IPB and 0.12 wt % copper NP were placed in the reactor. The reaction was performed at 30 and 60°C without initiator (azodiisobutyronitrile, AIBN). The reaction was stopped at the minimum rate of oxygen uptake  $(10-15 \ \mu l \ min^{-1})$ , which is determined by the scale factor of the buret in the gasometric installation. In some cases, repeated oxidation was performed 24 h after the end of the first

<sup>&</sup>lt;sup>1</sup> Electric-explosion Cu NPs were obtained at the Institute of High-Current Electronics, Siberian Division, Russian Academy of Sciences, Tomsk; mechanochemical Cu NPs, at the Institute of Solid-State Chemistry and Mechanochemistry, Siberian Division, Russian Academy of Sciences, Novosibirsk.

Powder	Preparation technique	$E/E_{\rm s}^{*}$	$s_{sp},$ m <sup>2</sup> g <sup>-1</sup>	Medium	Additive	Time of MT, min	W <sub>max</sub> ,** µl min <sup>-1</sup>	Induction period, min
Cu 8	EEC	1.0	8.7	Nitrogen	_	_	335	_
Cu 11	EEC	1.2	6.0	Xenon	—	_	300	_
Cu 13	EEC	0.8	2.2	Argon	—	_	100	_
Cu 18	EEC	2.0	2.1	Nitrogen	_	_	100	_
Cu 18(2)	EEC	2.0	9.7	Nitrogen	_	_	365	_
Cu 19	EEC	1.0	5.6	Nitrogen	_	_	280	_
Cu I	MT	] _	3.2	Air	$H(CF_2CF_2)_2CONH_2$	10	_	19
Cu II	MT	_	3.9	Air	H(CF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> CONH <sub>2</sub>	20	_	17
Cu III	MT	_	5.2	Air	H(CF <sub>2</sub> CF <sub>2</sub> ) <sub>2</sub> CONH <sub>2</sub>	30	_	6
Cu 1	MT	_	4.3	Air	CuCl <sub>2</sub>	10	_	_
Cu 2	MT	-	6.2	Air	$CuCl_2$	20	_	_
Cu 3	МТ	_	6.9	Air	CuCl <sub>2</sub>	30	_	_

**Table 1.** Physicochemical parameters and preparation conditions of copper nanopowders

\* E, supplied energy;  $E_{\rm s}$ , energy of metal sublimation. \*\*  $W_{\rm max}$ , maximum rate of oxygen uptake.

oxidation. Liquid reaction products (acetophenone, AP, and dimethylphenylcarbinol, DMPC), were analyzed by gas-liquid chromatography on a Perkin-Elmer Sigma 2B chromatograph with a flame-ionization detector on an SE-52 column (column length 33 m) in the programmed-temperature mode: initial thermostat temperature 80°C, temperature raised at a rate of 3 deg min<sup>-1</sup> to 150°C. Carrier gas helium. Quantitative analyses were performed with an internal reference (n-hexane). IPB hydroperoxide (IPB HP) was determined iodometrically by the standard procedure [9].



Fig. 1. Rate W of oxygen uptake vs. time t in oxidation of IPB in the presence of nanopowders. Nanopowder: (a) (1) Cu 8, (2) Cu 11, and (3) Cu 13; (b) Cu II. Temperature 60°C; the same for Fig. 2.

X-ray diffraction analysis was made on a DRON-1 instrument with a cobalt radiation source.<sup>2</sup> The X-ray diffraction patterns were recorded by point-by-point scanning with a step of  $0.05^{\circ}$ , with recording into a file for further computer processing.

The efficiency of copper NPs as catalysts for IPB oxidation was judged from the rate of oxygen uptake by a system constituted by IPB and Cu NP. Figure 1a shows the most typical kinetic curves of oxygen uptake in oxidation of IPB in the presence of 0.12 wt % Cu NP produced by EEC in various inert gases. Curves 1 and 2 are characteristic of Cu NP possessing a sufficiently large specific surface area [Cu 18(2), Cu 8, Cu 19, and Cu 11]. The run of the kinetic curves is about the same irrespective of the medium in which a powder was obtained: an exceedingly high rate at the beginning of the reaction and an abrupt fall in 10-15 min (Fig. 1). In the system constituted by IBP and Cu 13 NP with a small specific surface area  $(S_{sp} = 2.2 \text{ m}^2 \text{ g}^{-1})$ , oxygen is taken up at a low rate during the entire reaction course (Fig. 1, curve 3). For Cu NP produced by EEC, the following tendency can be noted: the larger the specific surface area of Cu NP, the higher the rate of oxygen uptake by the system constituted by IBP and Cu NP (Table 1).

A somewhat different behavior is exhibited in IBP oxidation by Cu NP produced mechanochemically. Irrespective of an additive, the rate of oxygen uptake gradually increases with time (Fig. 1b), with this type of curves characteristic of all mechanochemical Cu

<sup>2</sup> X-ray studies were carried out at the Institute of Strength Physics and Materials Science, Siberian Division, Russian Academy of Sciences, Tomsk.

Dowdor	Yie	eld, %		Conversion, %	Concentration of	Oxidation tem-
rowdei	IPB HP	AP	DMPC		copper powder, %	perature, °C
Cu 8	0.53	0.30	0,35	1.18	0.12	60
Cu 11	0.6	0.32	0.44	1.36	0.13	60
Cu I	0.59	0.77	1.00	2.36	0.12	60
Cu II	0.8	0.88	1.25	2.93	0.12	60
Cu III	0.69	0.5	0.64	1.83	0.14	60
Cu 0	_	_	_	_	_	60
Cu 0	Trace amounts	—	_	-	-	80
Initiator	1.75	_	_	_	0.12	60

Table 2. Composition of products formed in isopropylbenzene oxidation in the presence of a copper nanopowder

NPs. The powders are as if "shaken up" in the course of time. The oxygen uptake in IPB oxidation in the presence of mechanochemical Cu NP begins only after a certain induction period (Table 1).

The time in which the minimum rate of oxygen uptake  $(10-15 \ \mu \text{l min}^{-1})$  is reached depends on the method by which Cu NPs are obtained: for NP produced by EEC, the minimum oxidation rate is reached rather rapidly (in 30–40 min), and this occurs the faster, the larger the specific surface area of the powder. For mechanochemical Cu NP, the time in which the minimum rate of oxygen uptake is reached is long and independent of the specific surface area of the powder. After the minimum rate of oxygen uptake is reached, the reaction may continue during an infinitely long time until the whole amount of IPB enters into the reaction or the reaction terminates because of recombination processes.

IPB oxidation in the presence of a Cu powder with a particle size of 40  $\mu$ m and a specific surface area of 0.016 m<sup>2</sup> g<sup>-1</sup> (Cu 0) deserves separate consideration. Copper with such a specific surface area does not catalyze the IPB oxidation at 60°C. At 80°C, the reaction starts in 15 min, and then oxygen is adsorbed at a very low, nearly constant rate.

A chromatographic analysis of the reaction products formed in IPB oxidation in the presence of Cu NP demonstrated the presence of not only IPB HP, but also AP and DMPC (Table 2), irrespective of the preparation method, specific surface area, preparation medium, and other physicochemical properties of NP (Table 1). When used in the form of shavings, metallic copper decomposes hydroperoxides [10]; probably, the same behavior is characteristic of Cu NPs because it was impossible to selectively obtain only IPB HP in the presence of Cu NP. For electric-explosion Cu NPs, which have a large specific surface area and exhibit a high rate of oxygen uptake at the beginning of the reaction, the amount of reaction products is insignificant, in contrast to those characteristic of mechanochemical Cu NPs, at the same oxygen uptake. For example, the conversion is 1.36% (0.60 IPB HP, 0.32 AP, 0.44 DMPC) for electric-explosion copper Cu 11 with a specific surface area of 6 m<sup>2</sup> g<sup>-1</sup> and 2.9% (0.80 IPB HP, 0.88 AP, 1.25 DMPC) for mechanically treated Cu II NP. An increase in the mass of Cu NP by a factor of nearly 10 does not lead to any significant rise in the yield of the reaction products.

It is known [11] that IPB oxidation in the presence of a copper catalyst occurs by the radical-chain mechanism, with the primary radicals appearing on the surface of copper. This makes it possible to suggest a heterogeneous-homogeneous mechanism of the reaction by the scheme

$$\begin{split} (M) \ + \ O_2 \ \to \ (M^+) \cdots (O-O)^-, \\ (M^+) \cdots (O-O)^- \ + \ RH \ \to \ (M^+) \ + \ (OOH)^- \ + \ R^{\bullet}, \\ (M^+) \ + \ (OOH)^- \ \to \ (M) \ + \ HO_2^{\bullet}, \qquad (1) \\ HO_2^{\bullet} \ + \ RH \ \to \ H_2O_2 \ + \ R^{\bullet}. \end{split}$$

The performance of a catalyst depends on the rate at which the active centers on the catalyst surface can adsorb reactants, retain them during the chemical transformation, and then release the reaction products to be free to perform a new catalytic cycle [1].

Probably, fast sorption of oxygen at the first instant of time is natural for Cu NPs with a sufficiently large specific surface area. After the surface of copper is saturated with oxygen, the rate of uptake decreases significantly because three processes start to compete: oxygen uptake, formation of reaction products on the surface, and desorption of the reaction products into solution. Chromatographic analysis for the reaction products, made immediately after the reaction ter-

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**Fig. 2.** Rate W of oxygen uptake vs. time t in oxidation of IPB in the presence of (a) Cu 8 and (b) Cu I nanopowders. Oxidation: (1) first and (2) repeated in 24 h.



**Fig. 3.** X-ray diffraction patterns of Cu 11 powder (*I*) before and (2) after the oxidation. (*I*) Intensity and (2 $\theta$ ) Bragg angle.

minated, reveals trace amounts of AP and DMPC. This means that the oxygen sorption is faster than formation of the reaction products and their desorption from the surface into the bulk. Nevertheless, after a certain time, when all the products would have diffused from the surface into the bulk, the conversion in the oxidation in the presence of electric-explosion Cu NPs with a large specific surface area is considerably lower than that with mechanochemical NPs. Probably, part of oxygen involved in oxidation is irreversibly sorbed on these NPs. Repeated oxidation of the system constituted by IPB and Cu NPs was performed in 24 h. The rate of oxygen uptake in the repeated oxidation of the system constituted by IPB and Cu NP prepared by the EEC method is always lower than that in the first oxidation of the same system, irrespective of the specific surface area of the NP (Fig. 2a). This means that the surface is not "freed" of oxygen even in the course of time. The curve of oxygen uptake in the repeated oxidation in the presence of mechanochemical Cu NP runs somewhat higher than that of the first oxidation (Fig. 2b). It was assumed that oxygen is consumed for oxidation of copper, and an X-ray diffraction analysis was carried out. However, an X-ray diffraction analysis did not reveal any additional formation of copper oxides after the reaction. Oxygen sorbed on the surface does not oxidize copper, but, probably, can be rather firmly retained on the surface of powder particles, without being involved in IPB oxidation to give reaction products; for example, it may form charge-transfer complexes with copper.

Figure 3 shows X-ray diffraction patterns of Cu 11 NP before and after the oxidation. The patterns reveal no difference between the structures of the initial NP and that isolated after the reaction. For example, the lattice constants (fcc unit cell) differ by less than 0.01% and the size of crystallites, determined from the angular broadening of the lines, was 60 and 62 nm in the initial and treated states, respectively. The only difference that could be revealed in the X-ray diffraction patterns is that the intensity of weak lines at  $40^{\circ}$ – $48^{\circ}$ , which, according to a phase analysis made on the basis of the ASTM file, belong to CuO (tenorite structure, 41-254 card), changes: after treatment of the powder, their intensity increases.

It was of interest to reveal the nature of the active center in Cu NPs, which can activate oxygen by scheme (1) and give rise to radical-chain transformations. A study was carried out<sup>3</sup> in order to elucidate the reasons for the increase in the reactivity of a mechanochemically treated copper powder, compared to the same powder in the initial state. It was demonstrated by X-ray photoelectron spectroscopy (XPS) that the intensity of oxygen peaks with a binding energy of 530.9–531.1 eV, which is not characteristic of adsorbed oxygen or copper oxides, increases in mechanochemically treated copper NPs [12]. The authors of this study believe that this peak may belong to the lattice, or suboxide, oxygen bound with defective sites in copper powder particles. In view of the fact that the bonding energy of the lattice oxygen exceeds that in the oxides CuO and Cu<sub>2</sub>O, it may be stated that the bonding of copper atoms with the lattice oxygen is largely covalent, i.e., the suboxide oxygen donates its excess electron density to a copper atom bonded with it. The authors assume that the role of active centers in a copper sample activated by

<sup>&</sup>lt;sup>3</sup> At the Institute of Solid-State Chemistry and Mechanochemistry, Siberian Division, Russian Academy of Sciences.

mechanical treatment or other methods leading to saturation with the lattice oxygen is played by oxygen atoms covalently bonded to copper atoms. Therefore, they suggest the following model of interaction of such an active center with molecular oxygen:



The lattice oxygen donates its excess electron density to the neighboring Cu atom, whose charge rapidly reaches the surface atom. The presence of an excess electron density on surface atoms leads to activation of molecular oxygen, which can then initiate radical-chain transformations in the catalytic oxidation of IPB.

The data of [12] can be used to explain the results obtained in this study. The copper NPs mechanically treated in ball mills in air probably contain a larger amount of suboxide oxygen capable of formation of active centers giving rise to radical chain reactions, because a 2 times greater amount of reaction products is formed. In addition, it is possible that the mechanochemical Cu NP treated in the presence of organic additives has on its surface a smaller number of free active sites at which oxygen not involved in the oxidation could be adsorbed. This is so because these sites, represented by various dislocations and structural surface defects, are already occupied in part by surfactants (e.g., by an organic surfactant, 2,2,3,3, 4,4,5,5-octafluorovaleramide), which can themselves form complexes with copper.

For copper NP produced by EEC in an inert atmosphere, presence of a large amount of suboxide oxygen is unlikely, and, therefore, it may be assumed that most part of absorbed oxygen is not activated and is not involved in the oxidation, being irreversibly sorbed at defective sites on the surface.

## CONCLUSIONS

(1) In oxidation of isopropylbenzene in the presence of electric-explosion copper nanopowders obtained in an inert atmosphere, the maximum rate of oxygen uptake depends on the specific surface area of the nanopowders. The rate of oxygen uptake in the first oxidation run exceeds that in the case of a repeated oxidation run.

(2) With mechanochemically produced copper nanoparticles, the rate of oxygen uptake in the re-

peated oxidation runs exceeds that in the first oxidation of isopropylbenzene, which may be due to the high degree of caking of these powders and their "shake-up" in the course of time.

(3) The final products are isopropylbenzene hydroperoxide, acetophenone, and dimethylphenylcarbinol. The relative amounts of the reaction products depend on the method used to produce the nanopowders.

(4) A possible mechanism of isopropylbenzene oxidation in the presence of Cu nanopowders was suggested. This mechanism is associated with the presence of suboxide oxygen, which is involved in the oxidation and activates molecular oxygen.

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