

# Magneto-modified catalyst on the base of nanocrystalline CuO

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## Abstract

The weakly oxidized nanocrystalline copper powders of different sizes (average particle size of 30 and 100 nm) were used as the reactants at copper phthalocyanine (PcCu) formation. The nanocrystalline cupric oxide located at the particles surface serves as a heterogeneous magneto-controlled catalyst. A new effect of acceleration of chemical reaction rate controlled by low external steady magnetic field ( $\sim 2$  kOe) at room temperature was revealed and investigated on an example of formation of a coordination compound of PcCu. The rate of PcCu formation accelerated by 7–8 times after applying of a magnetic field.

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## 1. Introduction

An important feature of the strongly correlated systems based on the cuprates and manganites is the existence of strong interplaying between the spin, charge and orbital degrees of freedom [1–3]. In the low-doping case by carriers in the system the non-homogeneous electron (or charge) phase separation is arisen. The physicochemical peculiarities of such heterogeneities could be controlled by, for instance, temperature or magnetic field and these sites can operate as an active centers in the catalyst chemistry, adsorption and others. However up to now there is no investigation in that area.

It is extremely attractive from both fundamental and application view points to use the external steady magnetic field for tuning of spin and charge states of strongly correlated systems to control the reactivity of nanocrystalline solids at realization of chemical reactions.

In this connection, special attention should be given to the features of structure, charge and magnetic states of the low-dimensional antiferromagnetic and semiconductor CuO with non-stoichiometric composition [4]. In a bulk state an excessive solubility of oxygen in copper oxide is extremely small. The enhancement of solubility in nanocrystalline CuO may take place and greatly increase the number of carriers (electrons or holes) depending on the oxygen concentration.

The non-stoichiometric nanocrystalline copper oxide located, for instance, at the surface of the copper particles serves as a heterogeneous *magneto-modified catalyst* (MMC) whose reactivity could be controlled by magnetic field [5].

## 2. Experimental

The initial reactants in copper phthalocyanine (PcCu) synthesis ( $4\text{C}_8\text{H}_7\text{N}_3 + \text{Cu} + (\text{CuO-MMC}) \rightarrow \text{C}_{32}\text{H}_{16}\text{N}_8\text{Cu}(\text{PcCu}) + 4\text{NH}_3$ ) were 1,3-diiminoisindolenine (AII- $\text{C}_8\text{H}_7\text{N}_3$ ), solvents  $\pi$ -xylene and methanol (in a 30:1 ratio) and weakly oxidized copper nanocrystalline powders (NP) or iron-doped copper (Cu–Fe) nanopowders.

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External magnetic field was applied and then removed at RT to the Cu NP before the chemical reaction. The reference Cu NP was not subjected to magnetic field. For definiteness, the magnetic field strength and the duration of exposure were fixed to be 2 kOe and 1 min, respectively. Copper NP containing copper oxides were prepared using gas-condensation and electrical wire explosion methods. Control over the course of the reaction and characterization of phthalocyanine products was carried out by the electron absorption spectroscopy (EAS), IR, elemental, X-ray phase analysis and others.

### 3. Results and discussion

In the absence of magnetic field at any combinations (AII + NP + solvent) the rate of the reaction of PcCu formation was approximately constant.

A very clear chemical response (acceleration of chemical reaction rate) as a result of the magnetic field influence on the oxidized Cu NP was registered. It is an outstanding experimental fact that a short-term application and then removal of a magnetic field is sufficient to initiate the reaction. The required time to complete the reaction (PcCu yield  $\geq 90\%$ ) after magnetic treatment depends on the phase composition and size particles.

In the Fig. 1 the ratio of intensities of the EAS lines measured for final solid products (PcCu) of reaction using the gas-condensation NP samples (30 and 100 nm) under the field and without it (Fig. 1c) are given. Intensity of the absorption lines is proportional to concentration of PcCu ( $\beta$ -phase). After magnetic field treatment of copper NP (average size 100 nm and

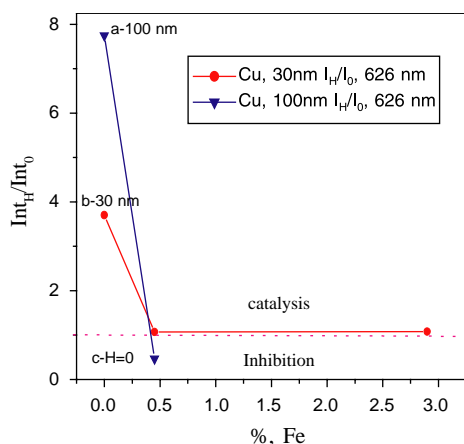


Fig. 1. The ratio of line intensities for typical of wave length of PcCu (626 nm) in EAS spectra for the ended products (in 130 days) for magnetized (a, b) and non-magnetized (c—dotted line) of oxidized Cu powders (30 and 100 nm) versus Fe content in copper.

content of Cu oxides  $\sim 9\text{wt}\%$ ) the rate of PcCu formation is increased by 7–8 times (see Fig. 1, a–100 nm). The PcCu yield for the Cu-100 nm after applying of magnetic field was more than 90%. At the same time the concentration of PcCu for NP Cu-30 nm was twice less (Fig. 1, b–30 nm). The results obtained from the ratio of intensity absorption lines and weighing of the final solid products (PcCu) for NP Cu (30 and 100 nm) well agreed with each other. Doping nano-Cu with iron completely (see Fig. 1) suppresses the magnetic field effect.

The most consistent approach applicable for the explanation of magnetic field-controlled reactivity could be a model of strongly correlated polar pseudo-Jahn–Teller (PJT)-centers [3]. The existence of the (PJT)-centers (hole  $[\text{CuO}_4^{5-}]$  and electron  $[\text{CuO}_4^{7-}]$  centers) can be caused by the appearance of charge carriers due to non-stoichiometry of nano-CuO. In fact, the optical absorption spectra in infra-red range (up to 3 eV) display the essential increase of the numbers of the hole and electron centers in the nanocrystalline cupric oxide.

The existence and quantum behavior of the specific tunnel paramagnetic centers with special valence and hysteresis spin states enables to qualitatively understand the reactivity change of CuO nanopowders under applying of magnetic field [6].

Many problems are yet left to be solved, which might help to both understand and clarify the fundamental nature of the new effect and to ensure their successful application. The magnetic phase diagram of non-stoichiometric CuO oxide in the wide-temperature range is not fully understood and it is not clear how it will be modified for nanoscaled particles. Evidently the detailed physical and chemical mechanisms that are responsible for the changing of reactivity of nanocrystalline cuprates (or other strong correlated systems) require more deep investigation in further.

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