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Nanoscale Copper Particles Derived from Solvated Cu Atoms in the Activation of Molecular Oxygen

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Nanostructured Cu powders ranging from 3 to 4 nm in diameter have been prepared by the clustering of acetone solvated Cu atoms obtained via metal vapor synthesis (MVS). The copper nanoparticles are valuable catalytic precursors for the oxidation with molecular oxygen of a wide range of organic substrates under mild conditions and are largely more efficient than commercial Cu samples.

Introduction

Active metals are of large interest in preparative chemistry and catalysis.[1] Their behavior is strongly related to the particle size distribution, and nanostructured metals are expected to have unusual electronic, optical, magnetic, and chemical properties, different from those of atomic or molecular species and bulk metals.[2] Chemical reduction of transition metal salts,[3] electrochemical methods,[4] ultrasounds,[5] and metal vapor chemistry[6] are promising preparative routes to these materials.

In preparative routes involving metal vapor as reagents, acetone was found to be a suitable organic ligand to prepare Au colloids from the corresponding solvated intermediates.[7] We report here that the reaction of Cu atoms with acetone and the further clustering at room temperature affords nanostructured Cu particles, averaging 3−4 nm in diameter, which are efficient catalytic precursors for the oxidation of organic substrates with molecular oxygen.

Experimental Section

Copper “commercial” (99%, RPE, from Carlo Erba) and copper “bronze” (99% for organic synthesis, from Aldrich) were used. Phenol, methanol, and pyridine (distilled and stored on KOH) had the highest purity grade from Fluka. Gaseous oxygen, from Rivoira, was 99.99% pure.

^{1}H NMR spectra were performed in $CDCl_3$ solution on Varian 300 spectrometer, and mass spectra were performed using a VG analytical 70/70E spectrometer.

Copper metal (0.25 g) loaded into a Sylvania W/Al_2O_3 crucible was evaporated over a 1 h period, under a dynamic vacuum of ca. 10^{-4} Torr, and co-condensed with acetone (80 mL) at liquid nitrogen temperature, using a typical glass metal atom reactor.[8] The solid red-brown matrix obtained was allowed to melt, and the resulting brown solution was siphoned out under argon into a Schlenk flask. Acetone evaporation afforded 0.2 g of Cu powder.

Electron micrographs were obtained with a JEOL 2000EX microscope equipped with polar piece and top entry stage. Before introduction in the instrument, the samples were ultrasonically dispersed in isopropyl alcohol and a drop of the suspension was deposited on a copper grid covered with a lacey carbon film. The histograms of the metal particle size distribution for the Cu sample prepared via metal vapor synthesis, Cu MVS, were obtained by counting at least 300 particles onto the micrographs. The mean particle diameter (d_m) was calculated by using the formula $d_m = \Sigma d_i n_i / \Sigma n_i$, where n_i is the number of particles with diameter d_i.

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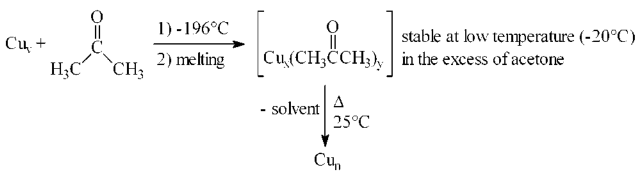
Scheme 1



The oxidation reactions were carried out in a 25 mL thermostated (ca. 25 °C) Carius tube connected with a large reservoir containing oxygen at 101 KPa and under magnetic stirring. In a typical run, phenol (940 mg, 10 mmol), pyridine (2.4 g, 30 mmol), and commercial or MVS copper (13 mg, 0.2 mmol) in 10 mL of methanol were reacted for 24 h with molecular oxygen. The solvents were evaporated in vacuo, and the crude reaction was purified by flash chromatography. The products were characterized by MS and ^{1}H NMR analysis, and the data were consistent with those reported in the literature.

The reactions performed at 70 °C were carried out using a stainless steel autoclave thermostated with an oil bath.

Results and Discussion

Copper nanoparticles have been generated by the clustering of acetone solvated Cu atoms. The reaction of Cu vapor with acetone at −196 °C affords a red-brown solid matrix which on melting gives acetone solutions of Cu atoms which are stable at low temperature (−30 °C). Warming to room temperature and evaporation of solvents provides ultrafine Cu powder (Scheme 1).

TEM analysis showed that the Cu powder is constituted by very small particles, aggregated to form spongy ensembles smaller than 200 nm in size. TEM observation of the border region of the aggregates at higher magnification evidenced that most of the single particles are well shaped and feature well-defined edges (Parts a and b of Figure 1). The statistical analysis of the dimensions of these particles resulted in a particle size distribution in the $1.5 < d < 7$ nm range, with mean particle size $d_m = 3.6$ nm (Figure 2). The morphological features of the Cu vapor derived powders have been compared with those of two commercial Cu samples: copper commercial (99%, RPE, from Carlo Erba) and copper bronze (99% for organic synthesis, from Aldrich).

The TEM analysis of the commercial Cu powder evidenced that such material is constituted by particles larger than 1 μm in size. Such particles appeared massive and quite regular in shape, as shown in Figure 3, where the TEM image of part of one of these particles is reported.

In the copper bronze sample, on the contrary, the TEM analysis indicated the presence of a nanostructural aggregation, with particle size averaging 20 nm in diameter (Figure 4).

The marked differences in the sizes of the particles gathered in aggregates in Cu MVS and Cu bronze powders and in the massive ones present in the commercial Cu sample should result in significant differences in the specific surface areas (SSA) of the three powders. The measurement of SSA for copper requires a specific apparatus for N_2O dissociative adsorption method, using a pulse-flow technique,[9,10] which is not easily available. However, some indication can be derived from TEM data, by calculating a SSA value on the basis of the mean size of the particles and assuming a geometrically defined particle shape. A good agreement between SSA values obtained by the N_2O dissociative adsorption method and SSA values derived from TEM data was found in previous studies on heterogeneous copper catalysts.[11] With the assumption of a spherical shape for particles in Cu MVS and Cu bronze, SSA values of 190 and 34 $m^2 \cdot g^{-1}$, respectively, were calculated, while a SSA value of 1 $m^2 \cdot g^{-1}$ was found for

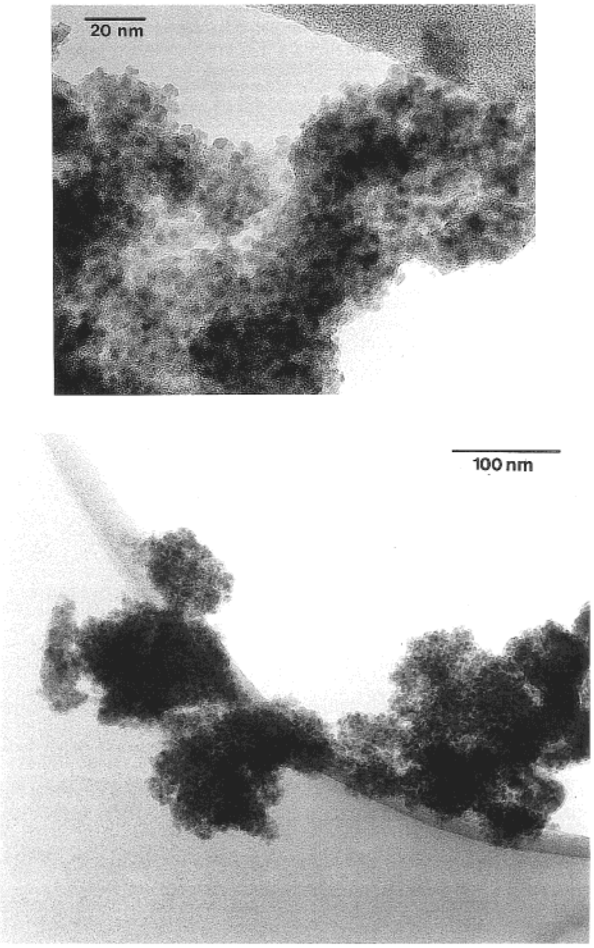


Figure 1. (a) Electron micrograph of the Cu$_{MVS}$ powder (magnification: ×200 000). (b) Electron micrograph of the Cu$_{MVS}$ powder (magnification: ×80 000).

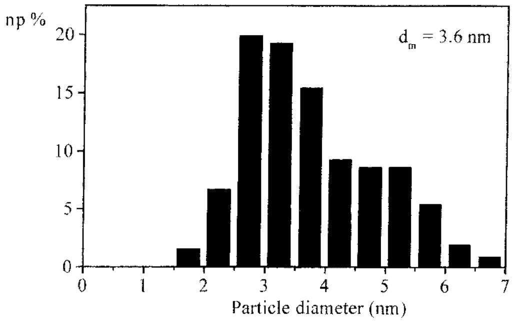


Figure 2. Particle size distribution of the Cu$_{MVS}$ powder.

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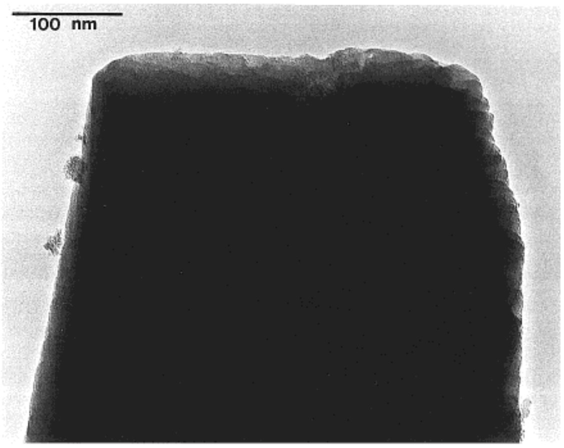


Figure 3. Electron micrograph showing a part of a particle in the commercial sample (original magnification: ×80 000).

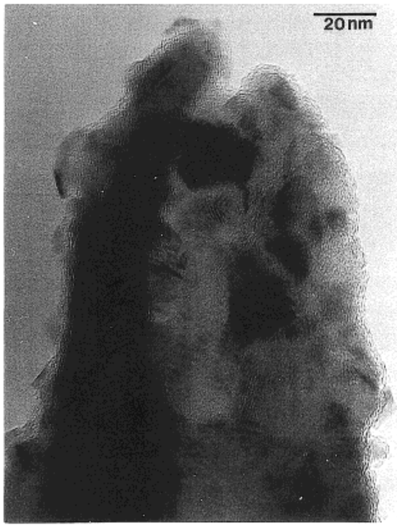


Figure 4. Electron micrograph of the Cu bronze sample.

Table 1. Morphological Characteristics of the Copper Powders

powder	morphological characteristics	aggregate size (μm)	particle diameter (nm)	SSA[c] (m^2g^{-1})
Cu MVS	spongy aggregates	~0.2	3.6[a]	190
Cu bronze	large aggregates with irregular shapes	>0.5	20[a]	34
Cu comm	massive with regular shapes	>10	~10^3 [b]	1

[a] As diameter (shape of the particles assimilated to a sphere; see Figures 1 and 4). [b] Side length (shape of the particles assimilated to a cube; see Figure 3). [c] Derived from TEM data.

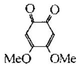
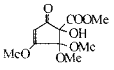
the commercial Cu sample, supposed to be formed by cubic particles with edge length of 1 μm.

The different characteristics of the copper powder, including the SSA derived from TEM data, are summarized in Table 1.

The actual SSA values for the Cu MVS and Cu bronze powders should be lower than the calculated ones, because of the aggregation of the particles. However, the texture of the aggregates observed in TEM images and the roughness of their borders allow us to propose that the SSAs of the three samples can be ordered in the series: Cu MVS > Cu bronze > Cu commercial.

To evaluate the role of the particle sizes of the Cu samples on their chemical properties, the oxidation of phenol with molecular oxygen, already well studied, using a 200−300 mesh commercial Cu powder,[12] has been examined as a reference reaction. The experiments were performed in MeOH, under reaction conditions quite similar to those adopted in ref 12.

Table 2. Oxidation of Phenol in the Presence of MeOH[a]

Entry	Catalyst	PhOH/Cu	T (°C)	Conv (%)	Products[b)]  **1**	 **2**	Specific activity[c)]
1	Cu comm.	50	25	8	74	26	4
2	Cu comm. (Copper bronze)	50	25	25	90	10	12.5
3	Cu MVS	50	25	81	96	4	40.5
4[d)]	"	50	70	90	90	10	46
ref 12a	Cu comm. 200-300 mesh	4	25	65	100	-	2.6
ref.12b	"	4	70	68	-	100	2.72

[a] Reaction conditions: 10 mmol PhOH; 0.2 mmol Cu powder, MeOH = 10 mL; Py = 3 mL; t = 24 h; T = 25 °C; [b] Satisfactory elemental analyses, mass spectra, and ^{1}H NMR data were obtained. [c] mol of product/g·atom of metal. [d] T = 70 °C; P_{O_2} = 12 atm (starting pressure), t = 3 h.

The results are summarized in Table 2.

It can be seen that MVS derived Cu powders are largely more active than Cu bronze and commercial Cu samples. With the use of MVS copper (entry 3), the conversion of phenol to 4,5-dimethoxy-1,2-benzoquinone, **1** (96%), and 1-hydroxy-2-oxo-4,5,5-trimethoxycyclopent-3-ene-1-methylcarboxylate, **2** (4%), is, at 25 °C and atmospheric pressure of O_2, 81% after 24 h. Under the same reaction conditions, the Cu bronze is less active (entry 2) while the commercial Cu sample (entry 1) is quite inactive. The oxidation with MVS Cu performed at 70 °C and P_{O_2} = 12 atm (entry 4) is almost complete after 3 h.

The reverse selectivity at 70 °C observed in the experiment reported in ref 12b can be reasonably related to the low ratio of PhOH/Cu used, which at that temperature can favor the further oxidation of **1** to **2**.

In oxidation reactions catalyzed by Cu powders, the interaction of molecular oxygen with Cu to form a layer of atomic oxygen is assumed to be a crucial step.[13] The specific particle sizes and the surface structures of the MVS derived naked Cu samples probably play an important role in this activation process, making these catalysts largely more efficient than the commercial ones, as was also observed for other metal vapor derived catalysts,[14] and more attractive than samples prepared

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in the presence of surfactants as stabilizers,[2b] which can strongly limit the catalytic properties.[15]

Preliminary experiments indicate that acetone solvated derived Cu and Fe powders are valuable catalytic precursors for the oxidation of a wide range of other organic substrates, such as cycloalkanes, cycloalkenes, thioles, and propargyl alcohols.[16] Considering that sonically generated nanostructured metals and alloys (Fe, Co, Ni, Fe/Ni) have been recently reported to be superior catalysts for the aerobic oxidation of cycloalkanes under mild conditions,[17] it is reasonable to believe that naked nanoscale metal particles could have an interesting future as valuable oxidation catalysts.

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