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Ball Milling of Copper Powder Under Dry and Surfactant-Assisted Conditions—On the Way Towards Cu/Cu₂O Nanocatalyst

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Samples of copper powder was milled with varied grinding frequencies in the presence of various organic agents (oleylamine, ethylene glycol or dimethyl sulfoxide) or without additives. The effects of experimental conditions were investigated by X-ray diffractometry, scanning electron microscopy and dynamic light scattering measurements. The aggregation of particles were supressed by added organics. The catalytic activities of the variously treated samples were measured in the Ullmann-type reaction of iodobenzene and 1H-pyrazole.

Keywords: Cu Powder, Dry or Wet Milling, Aggregation Suppression by Organics, XRD-SEM-DLS, Ullmann Reaction.

1. INTRODUCTION

The main interest towards the use of copper nanoparticles and fine powders stems from their peculiar physical and chemical properties. They have increased surface area, controllable size and shape being crucial in their catalytic reactivities.^{1,2} Besides being used as catalysts, they are applied as ingredient of paints for centuries,³ ceramic capacitors⁴ and anti-corrosion/antibacterial coatings.⁵ Copper is frequently considered as a secondary option to replace silver, gold, palladium or platinum, especially in microelectronic applications.⁶ Due to its relatively high abundance (50 ppm) in the lithosphere of earth and its easy recyclability without loss in quality, copper could be economically and environmentally viable alternative of scarcer and more expensive precious metals.

Copper powders and nanoparticles have multifarious synthesis methods including chemical as well as physical routes. Chemical reduction with ultrasonic irradiation⁷

or in microemulsion⁸ is as typical as pyrolysis⁹ and electrolysis.¹⁰ Physical methods including laser ablation,¹¹ the atomization¹² and vacuum vapor deposition¹³ are also often used. The mechanochemical techniques can be regarded as mixed chemical and physical methods. The starting materials are deformed, welded, fractured and transformed to or reacted with other crystals due to the generated local high pressure and temperature from the kinetic energy of the grinding medium.¹⁴⁻¹⁶ The collisions result in continuous deformation and fracturing, and thus fine powder can be obtained. However, cold welding can have predominant role when the mechanical treatment reaches the adequate intensity and the agglomeration of the particles becomes the favorable process, especially for ductile and soft materials as metallic copper is. In order to prevent the sticking of the particles and stabilize them at the nanoscale, one can select either thermodynamic or kinetic way of stabilization. The former technique requires adding solutes to decrease the grain boundary energy, and, thus help the segregation of particles.^{17,18} In the other route, secondary particles are necessary to wedge between

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the grain and reduce their mobilities.^{19, 20} As the result of stabilization, the agglomeration processes are suppressed, and the unimodal dispersity of the milled powders can be enhanced.²¹

In experimental work leading to this contribution, highly viscous organic materials, oleylamine and ethyleneglycol surfactant and a frequently used organic solvent, dimethyl sulfoxide were added to the copper powders. The mechanochemical treatment was carried out in a mixer mill. In this mill type, the balls impinged from the rounded ends of the jars causing mill-dependent, characteristic deformations in the sample.²² Finally, the catalytic performance of dry- and wet-milled copper powders were tested in the Ullmann reaction of iodobenzene and pyrazole.^{23, 24}

2. EXPERIMENTAL DETAILS

2.1. Materials

In the experiments, copper powder 99% purity, average diameter <75 μ m, Sigma-Aldrich), dimethyl sulfoxide (99.9%, Sigma-Aldrich), 1-phenylpyrazole (97%, Sigma-Aldrich), iodobenzene (98%, Sigma-Aldrich), ethylene glycol (99,8% Reanal Private), 1H-pyrazole (98%, Alfa Aesar), sodium methoxide (98%, VWR International), benzene (99,9%, VWR International) and oleylamine (C18 content 80–90%, Acros Organics) were employed. All chemicals were used without further purification.

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2.2. Mechanical Treatment of Copper Powder

For the grinding of the copper nanoparticles, a mixer mill (Retsch MM 400) having two stainless steel with 50 cm³ grinding jars and two stainless steel grinding balls (volume: \sim 8.2 cm³, diameter: 25 mm) were applied. The mill was operated using constant ball/sample weight ratio (100), and 120 min milling time, and the grinding frequency was systematically varied between 3 and 21 Hz. Both dry and wet grinding was performed in air.

During the treatment, 0.6 g of copper powder was placed in the grinding jar. Wet grindings were carried out via adding oleylamine, ethylene glycol or dimethyl sulfoxide, between 1 and 200 μ l, to the reaction mixture. Following the milling, the particles were washed by acetone, collected on 0.45 μ m filter and stored in closed glass tubes under N₂ atmosphere.

2.3. Catalytic Test Reaction

The following reactant quantities were used: iodobenzene: 5 mmol; 1H-pyrazole: 7.5 mmol; Cu powder: 0.2 mmol; sodium methoxide: 10 mmol. The reactants were dissolved in 5 ml DMSO, and placed in a continuously stirred glass reactor with PTFE septum. The reaction mixture was heated to 130 °C in oil bath, and quantitatively analyzed using a gas chromatograph (Hewlett-Packard 5890 Series II). The gas chromatograph was equipped with flame ionization detector and the column was 50 m

long (Agilent HP-1). During the chromatographic measurement, the temperature was increased stepwise from 100 to 180 °C. Authentic samples were used to identify the starting materials and the product using benzene as the internal standard.

2.4. Methods of Structural Characterisation

Powder X-ray diffractograms were recorded on a Rigaku Miniflex II instrument in the $2\Theta = 5-80^{\circ}$ range using 4°/min scan speed and employing CuK α ($\lambda = 1.5418$ Å) radiation. The reflections of the prepared materials were identified using the JCPDS (Joint Committee of Powder Diffraction Standards) database.

A Hitachi S-4700 scanning electron microscope (SEM) was used to characterize the morphologies of the samples. Images were obtained at several magnifications and at 10 kV acceleration voltage. The surfaces of the samples were coated with thin gold layer in order to avoid charging. The elemental analysis was performed by energy dispersive X-ray analysis (EDX). The Röntec QX2 spectrometer (installed with Be window) was coupled to the microscope.

Malvern NanoZS dynamic light scattering (DLS) instrument with 4 mW helium-neon laser light source ($\lambda = 633$ nm) was applied to evaluate size distribution of the samples at room temperature. Detection was made in back scattering mode at 173° and the powders were ultrasonically dispersed in ethylene glycol.

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3. RESULTS AND DISCUSSION

3.1. XRD Analysis of the Dry- and Wet-Milled Cu Powders

The diffractograms of the dry-milled copper powders are depicted in Figure 1 with varying milling frequencies. Three reflections were observable, the (111), (200) and (220) they were, which confirmed that the face-centred cubic structure of the copper powder (JCPDS#04-0836) was intact after milling and other impurities, such as Cu_2O



Figure 1. XRD measurements of the dry-milled powder with various grinding frequencies (the indexed lines in the diffractogram are of Cu⁰).

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or CuO was not generated in detectable amounts during milling. The X-ray diffraction pattern at 0 Hz represents the as-purchased (and unmilled) commercial copper powder with an average grain size under 75 μ m (indicated on the label, possibly the grain consists of highly agglomerated particles); however, the calculated particle size was around 37 nm (it was obtained from the X-ray diffractogram). X-ray line profile analysis determines the sizes of coherently scattering domains, which is often in good correlation with the crystallite or subgrain sizes obtained by other characterising techniques like transmission electron microscopy. However, these numbers cannot be regarded as particle sizes, when the powder was prepared by plastic deformation.²⁵ The generated defect boundaries and the dipolar walls inside the grains provide smaller values than the real ones, as revealed by for instance the SEM images (they showed copper particles in the micrometer range). The size of coherently scattering domains was reduced monotonously by growing the grinding frequency from 3 to 12 Hz. On further increasing the frequency, this tendency slowed down. In order to avoid the amortization of the grinding jars, higher frequency than 21 Hz was not applied, and the wet milling experiments were performed at 12 Hz.

Applying dry milling, the ductile copper powders adhered, and formed thin foils on the internal surface of the grinding jars. The addition of organic liquids could prevent this phenomenon, the samples kept their powder consistency allowing easier handling. This observation was used in further experiments, the volume of the liquids applied were varied from 1 to 200 μ l, and in all cases, even 1 μ l proved to be sufficient to avoid foil formation.

The diffractograms registered after the addition of oleylamine (Fig. 2) and ethylene glycol (Fig. 3) displayed similar behaviour: the coherently scattering domain sizes grew permanently due to the increasing amount flexible organic molecules, which could absorb part of mechanical energy efficiently.



Figure 2. X-ray diffraction pattern of the wet-milled powders in the presence of oleylamine (the indexed lines in the diffractogram are of Cu^0).

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Figure 3. X-ray diffractograms of the wet-milled powders with ethylene glycol (the indexed lines in the diffractogram are of Cu^0).

During grinding, on liquid addition, copper(I) oxide was formed as a side product. The extent of oxidation increased on the increasing amount of organics to a point. The generation of Cu₂O (JCPDS#78-2076) reached the maximum at 25 μ l added organics in all diffractograms. When milling was performed in the presence of DMSO, its reflections (Fig. 4) were clearly observable to estimate its wt% from the integrated peaks intensities.²⁶ The crystalline phase of cuprous oxide was only 1 wt%, probably it is located on the surface of copper particles. Curiously, the sizes of coherently scattering domains have changed and followed maximum curve, which seemed to be contradicting to former experiences.

3.2. Characterization by Scanning Electron Microscopy

In order to follow the size and morphology alterations, SEM images of the milled powders were taken (Fig. 5). For the dry-milled samples, particles sizes varied in the 50–200 μ m range, which is larger than that of the initial



Figure 4. XRD study of the wet-milled powders with dimethyl sulfoxide (beside the indexed lines in the diffractogram are of Cu^0 , the lines of Cu_2O oxide also appeared).



Figure 5. SEM images of the milled powders: A—dry grinding, wet-ground samples in the presence of 25 μ l of organics: B—oleylamine, C—ethylene glycol, D—dimethyl sulfoxide.

powder. The reason is that the particles flattened due to the cold welding and the mechanical compressive stress. Using wet milling, the planar morphology with rounded edges remained; however, the average particle sizes were reduced under 30 μ m, especially on DMSO addition, where the size of larger part of the grains did not reach 10 μ m. These observations spectacularly indicate the stabilizing effect of added organic solvents, even that of dimethyl sulfoxide, which commonly is not considered to be a surface active agent. EDX measurements did not show any sign of iron atoms verifying that the grinding jars were not degraded at 12 Hz either under dry- or wet-milling conditions.

3.3. Size Distributions of the Milled Powders

From the commercial and dry-milled samples, we were unable to create stable, non-settling dispersion because of the voluminous particles obtained; however, the wet-milled powders could be dispersed successfully in 1 h continuous ultrasonic treatment in ethylene glycol (Fig. 6). The curves displayed bimodal distribution with progressively reduced particles sizes. Two main routes of mechanical energy mediation can be envisaged; the direct energy transfer between the powders and grinding medium (balls, inner surface of the jars) or the indirect one, when particles transfer their kinetic energy to other particles. The direct

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Figure 6. Bimodal aggregate intensity-weighted size distribution curves of wet-milled copper powders.

and indirect energy transfers are connected to elastic and inelastic collisions, respectively. In the latter, the soft and ductile copper particles absorbed a part of the energy and transferred a smaller proportion to deformations. These effects may induce the aggregation of the primary particles in two different size ranges. In the presence of oleylamine and ethylene glycol, these ranges were 2000–3000 nm and 250–400 nm. The distribution was bimodal in the presence of DMSO as well; however, the particles were smaller, around 800 and 140 nm. Applying 100 μ l DMSO the particle sizes further decreased under 100 nm. DLS measurements verified that the DMSO was an excellent stabilizing agent mitigating aggregation induced by cold welding or van der Waals interactions.

3.4. Catalytic Test

Derivatives of pyrazole are widely investigated as biologically active heterocyclic chemicals. They have potential in the synthesis of anti-inflammatory, antimicrobial agents, herbicidal or even A3 adenosine receptor antagonists.²⁷ In our work, the catalytic activity of the milled and commercial copper powders were compared in the Ullmanntype synthesis of 1-phenylpyrazole (Table I). The duration of the reaction was limited to 24 h, in longer runs, the

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maximum yield decreased due to polymerization of the primary product falling to zero after 48 h reaction time.

The untreated commercial copper powder was of low activity, which could be enhanced significantly (by more than three times) on dry milling. The activity of the catalyst could be enhanced further applying wet milling in oleylamine and even further using DMSO. The significant activity increase on using oleylamine may be connected to suppressing the aggregation processes, and thus, to the larger accessible catalytically active surface. This is a significant factor for the DMSO-milled materials as well; however, as it has been mentioned previously, Cu₂O was

 Table I. Ullman-type reaction of iodobenzene and 1H-pyrazole in the synthesis of 1-phenylpyrazole.



also formed on Cu particles during wet milling, and it is known to aid the synthesis.^{28–30} This promoting effect was the highest in DMSO indicating the presence of increased amount of Cu₂O phase as a side effect of wet milling.

4. CONCLUSIONS

By increasing the grinding frequency, the coherently scattering domain size was reduced monotonously; however, but the cold welding processes resulted in heavily aggregated particles, predominant during dry milling. Using added organics could decrease the aggregation tendency of milled copper powder. Dimethyl sulfoxide proved to be excellent protective agent, the as-prepared particles were generated in nano- or micrometer scale. Even dry milling was able to increase the catalytic activity; however, wet milling, especially in DMSO led to remarkable further increase due to the significant increase in the accessible active surface as well as the promoting effect of Cu_2O even if it was formed in minute amounts during milling.

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