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Preparation and Characterization of Copper Nanoparticles Stabilized by Poly(vinyl alcohol) for Catalytic Oxidation of 1-Propanol

The aqueous solution of copper (II) complex of poly(vinyl alcohol) (PVA-Cu(II)) was characterized by conductimetric titration, UV-Vis spectroscopy and FTIR. The molar composition of the PVA-Cu(II) complex was determined to be equimolar. Subsequently, the PVA-Cu(II) complex was reduced by sodium borohydride to prepare copper nanoparticles (CuNPs) stabilized by PVA (PVA-CuNPs). According to DLS measurements in aqueous solution the average size of PVA-CuNPs was varied from 10 to 25 nm depending on the amount of sodium borohydride used for reduction. The optimal volume of sodium borohydride to obtain 96 % PVA-CuNPs with 10 nm size was found to be 3 mL of $NaBH_4$ (0.5 mol·L^{-1}). The PVA-CuNPs were then deposited onto SiO_2 support to obtain SiO_2/PVA-CuNPs nanocatalyst for the oxidation of 1-propanol. The SEM image and XRD spectrum of SiO_2/PVA-CuNPs nanocatalyst showed the deposition of PVA-CuNPs on the surface of SiO_2. The resulting SiO_2/PVA-CuNPs nanocatalyst was used for the oxidation of 1-propanol to propionaldehyde by molecular oxygen in a batch-type catalytic reactor at 20°C and atmospheric pressure. The optimum catalyst mass and reaction time were found for the conversion of 1-propanol to propionaldehyde with yields ranging from 61.4 % to 87.8 %. Criteria of hydrodynamic and diffusive similarity (Re, Pr', Sh), overall volumetric mass transfer coefficient ($k_L a$), and economic metric (STY) were evaluated. 1-Propanol reacted with the decomposed atomically adsorbed oxygen atoms on the Cu(111), (220) surfaces to form propionaldehyde and water.

Keywords: copper nanoparticles, polyvinyl alcohol, metal-polymer complex, oxidation, 1-propanol, oxygen, heterogeneous catalysis, silica.

Introduction

The catalytic oxidation of alcohols plays an important role among organic transformations and continues to attract great attention [1]. The resulting carbonyl-containing compounds, such as aldehydes, can participate in further reactions important for fine chemical synthesis. Inexpensive air [2, 3], oxygen [4], hydrogen peroxide [5], and ozone [6] are commonly used as a source of oxygen atoms in the oxidation of 1-propanol to propionaldehyde and propionic acid. The ability of copper to adsorb, activate O_2 and generate copper-oxygen species in heterogeneous catalysts can explain their involvement in the four-electron processes in which O_2 and H_2O are interconverted [7, 8]. Copper nanoparticles are cost effective in comparison to noble d-metals such as Ag, Au and Pt. They are widely applied as catalysts in the coupling reactions, C–H bond activation reactions, oxidation and reduction reactions, and multicomponent reactions [9].

The two-phase (liquid-solid) and three-phase (gas-liquid-solid) stirred tank reactors, as a major class of multiphase reactors, are widely used in the chemical industry due to their operational reliability, flexibility and improved mass transfer. Three-phase systems are more complex than two-phase systems because the presence of the third phase affects the flow behavior existing in two-phase systems [10]. Three-phase stirred tank reactors are widely used in catalytic hydrogenation, oxidation, ammonolysis, fermentation, and wastewater treatment [11]. However, relatively little information is available on mixing in mechanically stirred three-phase gas-liquid-solid tank reactors [12, 13].

The combination of primary alcohols with environmentally friendly oxidants such as oxygen, air and hydrogen peroxide allows the production of carbonyl compounds mainly in continuous flow packed bed reactor systems. Control of the temperature of the oxidation reactions, minimization of the potential explosion zone inside the reactors and easy purification of the products are the main obvious advantages of continuous flow technology [14]. The liquid phase oxidation of aliphatic alcohols to aldehydes over heterogeneous catalysts is a well-known test reaction for multiphase reactors. When selecting a reaction system, mild operating conditions, high reaction rate, low cost and safety of reactants are key factors [15].

While two-phase processes can only be carried out in a flow-through reactor, three-phase processes can also be carried out in a batch-type reactor. The choice of reactor often depends on the type of oxidizing agent and its aggregate state. Two-phase liquid-solid systems are well known for the hydrogenation of organic substrates in the presence of immobilized metal nanoparticles [16–18]. Oxidation of various substrates in a conventional laboratory batch reactor is possible for both two-phase and three-phase systems. It was used as a two-phase liquid-gas or liquid-solid laboratory reactor for P-O coupling of yellow phosphorus with alcohols [19, 20], oxidation of octene-1 [21] and alcohols [22]. Selective oxidation of ethanol into acetaldehyde under mild conditions using a biocatalytic system based on cryogel-entrapped catalase can be an example of three-phase system (O_2-EtOH-cryogel) in batch-type reactor [23].

The aim of this work is preparation of copper nanoparticles stabilized by PVA followed by the deposition of CuNPs onto SiO_2 and evaluation of the catalytic activity of the SiO_2/PVA-CuNPs nanocatalyst in the oxidation of 1-propanol to propionaldehyde with a high yield.

Experimental

Materials

Chemically pure reagents $Cu(NO_3)_2 \cdot 2.5 \cdot H_2O$ (98 %), $NaBH_4$ (99 %), polyvinyl alcohol (PVA, Mw = 47000), silicon dioxide, 1-propanol (99.5 %), and hexane (99 %) were purchased from Sigma-Aldrich and used as received. Deionized water was used to prepare the solutions.

Methods

The pH-metric titration was performed on a pH-meter Bante-210 (China) with an accuracy of 0.02 pH units. The conductometric titration was carried out on the 856 Conductivity Module by Metrohm (Switzerland). FTIR spectra were recorded using Cary 660 spectroscopy (Agilent, USA) at room temperature within the 500–4500 cm^{-1} wavenumber range. UV–Visible spectra of the solutions were recorded using a UV–Vis spectrophotometer (Specord 210 plus BU, Germany). The average hydrodynamic size of the CuNPs was measured with a dynamic light scattering (DLS) instrument, Malvern Zetasizer Nano ZS90 (UK). PXRD patterns were collected on a Siemens/Brucker D5005 powder diffractometer using CuKα radiation in the 2θ range between 4° and 80° with a step width of $2\theta = 0.04°$ and a collection time of 10 s/step. Gas-liquid chromatographic analysis was performed on a DANI Master GC (Cologno Monzese, Italy). An Agilent 6890 N/5973 N gas chromatograph-mass spectrometer (Santa Clara, CA, USA) was used for the identification of the products. The morphology of CuNPs supported on SiO_2 was imaged using a SEM JSM-6390 LV (JEOL, Tokyo, Japan).

Preparation of Copper Nanoparticles

The nanosized CuNPs stabilized with PVA were prepared by the known procedure [24]. First, the PVA-Cu(II) complex was obtained in aqueous solution. Aqueous solutions of 0.25M $Cu(NO_3)_2$ (10 mL) and 0.5M PVA (Mw = 47,000) (10 mL) were mixed in the equimolar ratio $[PVA]:[Cu(NO_3)_2] = 1:1$. The resulting mixture was stirred for 5 min. Freshly prepared 0.5 M $NaBH_4$ (3 mL) was added dropwise to the light blue aqueous solution of PVA–Cu(II) and stirred for 1 h at room temperature. As a result, the turbid brownish-yellow solution of CuNPs stabilized with PVA (PVA–CuNPs) was prepared as shown in Figure 1 and then dialyzed for 24 h. After dialysis, the color of aqueous solution became transparent.

Depositing Copper Nanoparticles on Silicon Dioxide

PVA–CuNPs were deposited on SiO_2 by the impregnation method. For this 0.2 g of SiO_2 was added to 5 mL solution containing PVA–CuNPs and stirred for 5 hours. The precipitate was separated by preparative centrifugation using an “Eppendorf 5810R” (Germany) at 10×10^3 rpm. It was then washed by distilled water (150 mL×5) and filtered. The resulting amorphous mass was dried in a muffle furnace at 400–500^{o}C for 60 min to completely burn off the organic components (Fig. 1).

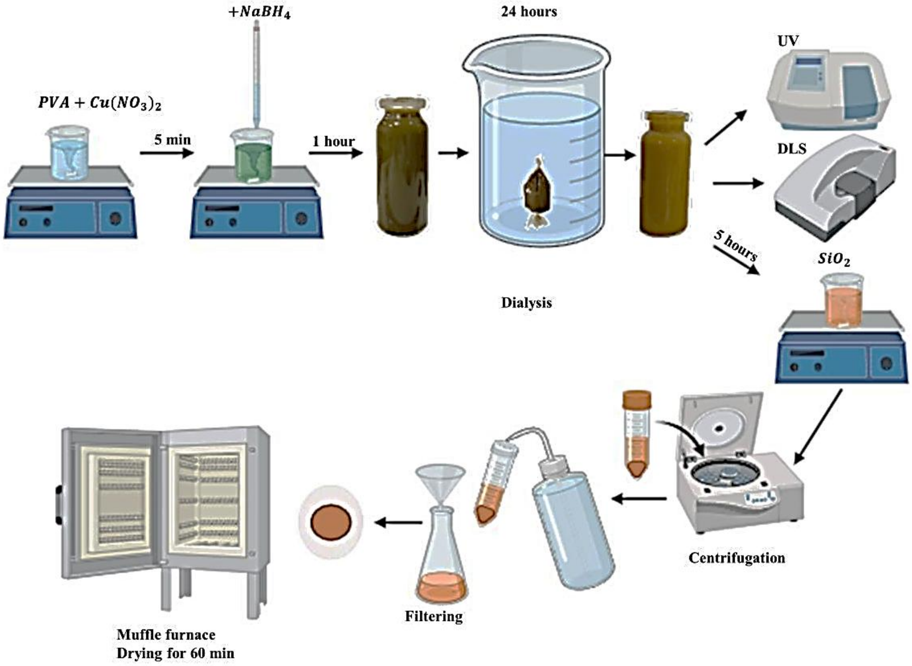
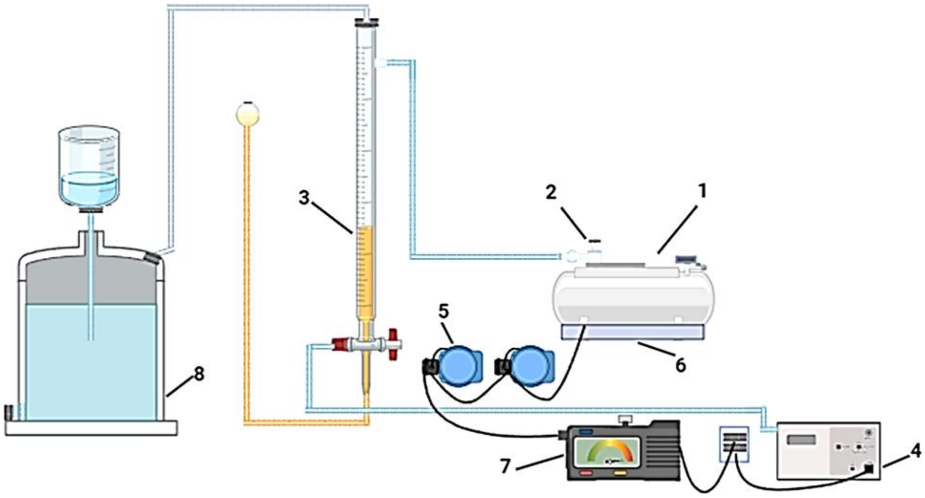


Figure 1. Preparation of CuNPs/PVA deposited on SiO_2

Oxidation of 1-Propanol in a Batch-Type Catalytic Reactor

The oxidation of 1-propanol was carried out in a thermostated glass batch reactor with a total volume of 150 mL (also called a catalytic “duck”) by molecular oxygen under aerobic conditions (Fig. 2). The kinetic reaction regime was achieved by shaking the reactor at a frequency of about 250–300 swingings/min. Dried copper nanoparticles in amounts of 0.1, 0.2, 0.3 and 0.5 mg were placed into the reactor. Then, 5 mL of 1-propanol and 5 mL of hexane were added to the reactor and thoroughly purged with oxygen for 5 minutes. The hexane was added to maintain the total solution volume at 10 mL and to use it as an extraction solvent to prevent moisture from entering the chromatography column. The experiment lasted 2–9 hours. The formation and accumulation of the product were monitored by checking its composition by GC analysis.



1 — catalytic “duck”, *2* — valve for catalyst and 1-propanol insertion, *3* — thermostated burette with dioxygen, 4 — thermostat, *5* — electric motor, *6* — shaker, *7* — laboratory autotransformer, *8* — Berzelius laboratory gasholder

Figure 2. Schematic view of a batch-type catalytic reactor setup for the catalytic oxidation of 1-propanol by molecular oxygen

Results and Discussion

UV-Vis Spectra and Conductimetric Titration

Figures 3 and 4 show the UV–V is spectra and the conductometric titration curve of the PVA-Cu(II) system. The appearance of absorption peak at λ = 800 nm for isomolar series of the mixtures of PVA and Cu(II) confirms the formation of coordination bonds between hydroxyl groups of PVA and copper(II) ions [25, 26]. According to the conductimetric titration curve, the composition of the PVA-Cu(II) complex is equimolar 1:1.

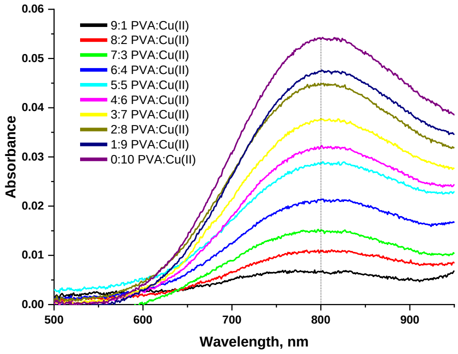


Figure 3. UV–Vis spectra of isomolar series of the mixtures of PVA and Cu(II). [PVA] = $1\cdot10^{-3}$ mol·L^{-1}; [Cu(II)] = $1\cdot10^{-3}$ mol·L^{-1}. V_{total} = 10 mL

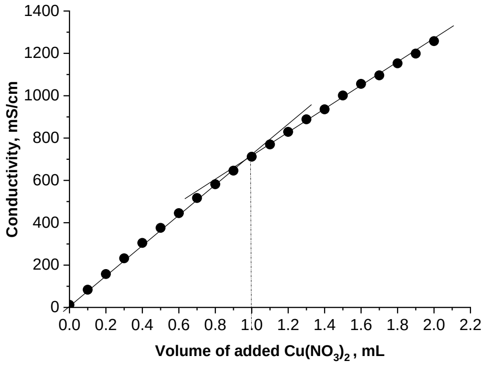


Figure 4. Conductimetric titration of PVA by Cu(II) in water. [PVA] = $1\cdot10^{-3}$ mol·L^{-1}; V_{PVA} = 10 mL; [Cu(II)] = $1\cdot10^{-2}$ mol·L^{-1}

FTIR spectra of the PVA and PVA–Cu(II) complex are shown in Figure 5. The broad peak at 3335 cm^{-1} corresponds to hydrogen bonded OH groups of PVA [27]. The band at 2937 cm^{-1} is related to CH stretching vibrations of macromolecular chain. The sharp band at 1091 cm^{-1} is attributed to the stretching mode of C–C groups, while two strong bands observed at 1456 and 864 cm^{-1} may be attributed to bending and stretching modes of CH_2 group, respectively. The broadening and shifting of the O–H stretching from 3335 cm^{-1} to 3381 cm^{-1} indicates the interaction of hydroxyl groups of PVA with copper ions.

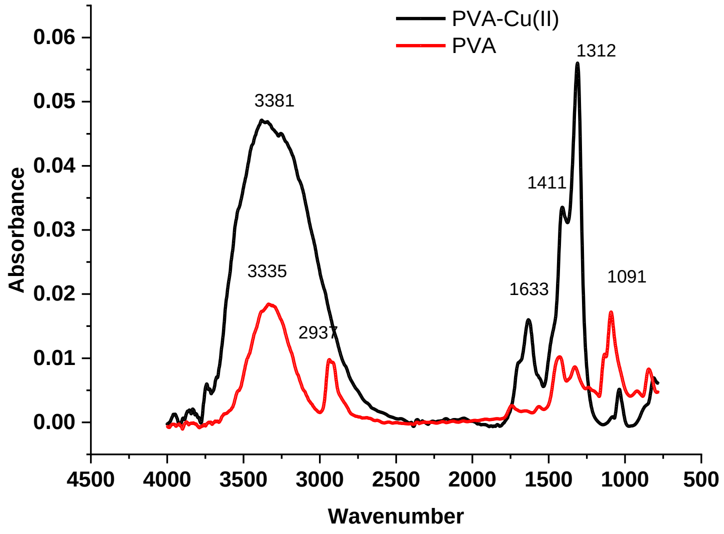


Figure 5. FTIR spectra of the PVA and PVA-Cu(II) complex

Reduction of Cu(II) to CuNPs by Sodium Borohydride

Sodium borohydride is a highly effective reductant with a standard reduction potential of E^o = –1.24 V [28].

$$NaBH_4 + 8OH^- \rightarrow NaBO_2 + 6H_2O + 8e^-;\ -1.24\left(E^0/V\right). \qquad (1)$$

In regard to the reduction potential difference between sodium borohydride and Cu(II), it has been demonstrated that sodium borohydride is capable of reducing Cu(II) to Cu(0) [29].

$$\mathrm{Cu}(\mathrm{II})(aq)+2e^{-}\rightarrow \mathrm{Cu}(s);\quad 0.34\left(E^{0}/V\right), \tag{2}$$

Cu nanoparticles were prepared by reducing Cu(II) ions with sodium borohydride ($NaBH_4$). The following reaction takes place in aqueous solution [30]:

$$4\mathrm{Cu}(\mathrm{II})+\mathrm{BH}_4^{-}+8\mathrm{OH}^{-}=4\mathrm{Cu}+\mathrm{B}(\mathrm{OH})_4^{-}+4\mathrm{H}_2\mathrm{O}, \tag{3}$$

Characterization of CuNPs by DLS

The average hydrodynamic sizes of CuNPs in aqueous solution vary from 10 to 25 nm (Fig. 6). In this case, particles with a size of 10 nm predominate, representing 96 % of the total. This value is between those of Cu MVS (Cu atoms obtained by metal vapor synthesis) and Cu bronze powders [31].

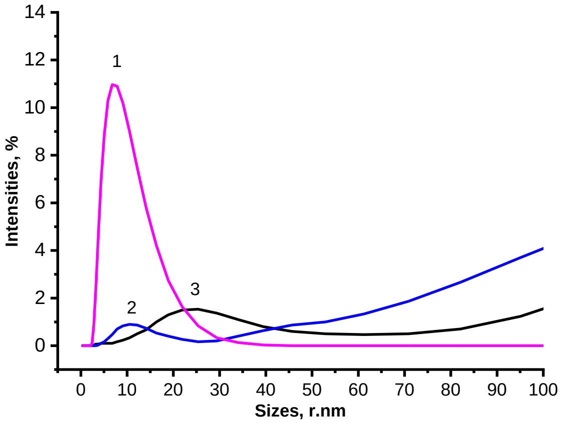


Figure 6. The average hydrodynamic sizes of PVA-CuNPs obtained by reduction of PVA-Cu(II) with 3 mL (1), 0.5 (2) and 0.25 mL (3) of $NaBH_4$ (0.5 mol·L^{-1})

Characterization of CuNPs by SEM and XRD

The surface morphology of the CuNPs deposited on SiO_2 is shown in Figure 7a. It can be seen that the CuNPs cover the surface of micron-sized SiO_2 [32].

The XRD pattern of CuNPs-SiO_2 is presented in Figure 7b. The diffraction patterns show the distinct peaks of two phases, namely crystalline copper metal (cubic) and Cu_2O (cubic), indicating the chemical reduction of Cu(II) ions to Cu and Cu(I). There are four peaks positioned at 2θ ~23°, 36.5°, 42.4° and 61.5°, which correspond well with (110), (111), (200) and (220) planes of the standard data for the face-centered cubic (FCC) structure of Cu_2O [33]. The XRD patterns also show the peaks for Cu at 2θ ~43.4° (111) and 74.3° (220). All peaks can be attributed to the cubic form of metallic copper [34, 35]. These peaks were remarkably close to those provided by JCPDS data of XRD for Cu_2O (JCPDS: 34-1354) and Cu (JCPDS: 04-0836).

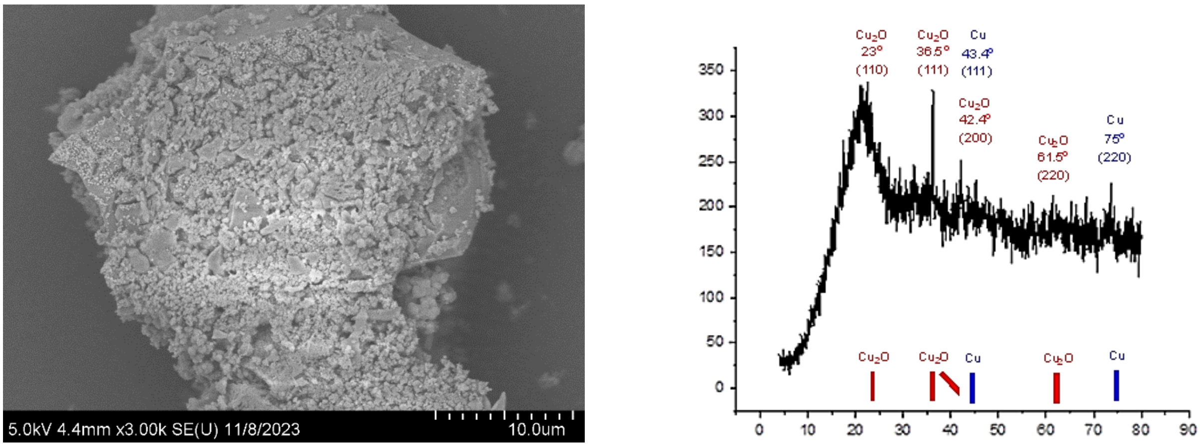


Figure 7. SEM micrograph (*a*) and XRD pattern (*b*) of CuNPs supported on SiO_2

The Oxidation of 1-Propanol

Copper nanoparticles prepared according to Figure 1 were used as a catalyst for the oxidation of 1-propanol with oxygen at 20°C and atmospheric pressure (Fig. 8).

$$\underset{\text{(liquid reactant)}}{\text{1-Propanol}} \quad + \quad \underset{\text{(gas reactant)}}{\text{Oxygen}} \xrightarrow[\text{CuNPs (solid)}]{20^{o}\text{C}} \text{Propionaldehyde} \quad + \quad \text{Water}, \tag{4}$$

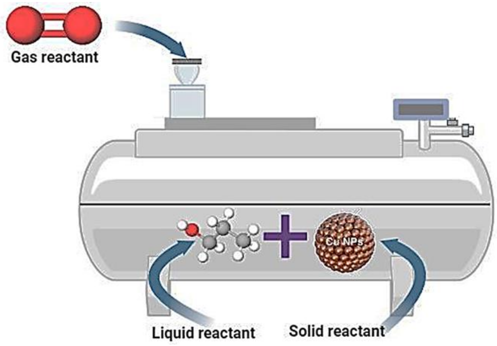


Figure 8. Three-phase system O_2–1-propanol–CuNPs

An increase in the mass of the catalyst (from 0.1 to 0.5 g) resulted in a notable enhancement in the conversion of 1-propanol, rising from 61.4 % to 87.8 % (Fig. 9). The conversion of 1-propanol exhibited a consistent trend over the course of the reaction, maintaining a constant level between 3 and 9 hours. After this period, a gradual decline was observed.

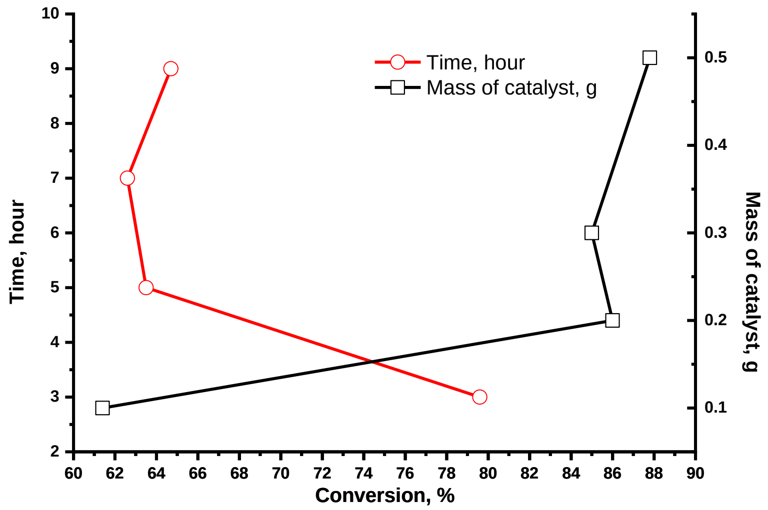


Figure 9. Mass- and time-dependent conversion of 1-propanol

The batch-type catalytic reactor containing the copper nanoparticles has a total volume of 150 mL and is composed of a glass cylinder with an internal diameter of 30 mm and a height of 132 mm. The reactor was equipped with a thermostatic jacket to maintain a constant temperature. The reactor performs a linear reciprocating movement and shakes at a frequency of approximately 250–300 swingings/min.

The Reynolds number in the shaking reactor was determined as Re = 5318, corresponding to turbulent flow (Table) [36, 37]. Shaking diameter of 25 and 50 mm had no significant influence on the mixing time [37]. After 3 hours of shaking the 1-propanol conversion decreased from 87.8 % to 61.5 % and did not change after 5, 7 and 9 hours. The results were mostly within a standard deviation of ±30 %. Using the equation for a Sherwood number ($Sh = 0.53Re^{0.54}\left(Pr'\right)^{0.33}$) for mass exchange, proceeding with solid phase, and a value for D_e found for the 1-propanol–hexane binary system was equal to $4.8 \cdot 10^{-8}$ $m^2 \cdot s^{-1}$, the mass transport coefficient (($\beta = 2.2 \cdot 10^{-4} \cdot s^{-1}$) was calculated as a function of the diameter of the shaking reactor.

In aerated bioreactors for gas–liquid–solid systems, the critical limiting factor for providing the optimal environment is the oxygen transfer rate (OTR). In shaking flask scale, oxygen transport is accomplished by the rotary or reciprocating action of a shaker apparatus [38]. Oxygen transfer (OTR, mmol·L^{-1}·h^{-1}) is most commonly characterized by the total volumetric mass transfer coefficient ($k_L a$, m·h^{-1}), which is the product of the liquid side mass transfer coefficient (k_L , m·h^{-1}) and the specific interfacial area of mass transfer (a, m^3·m^{-3}) [39]. The k_L value can be approximated by the Higby penetration mass transfer model [38].

Table

Engineering parameters of a batch-type catalytic reactor (V$_{total}$ = 150 mL) for 1-propanol oxidation

Metric	Value
$Re = \frac{w d_{reactor} \cdot {}^{20oC}_{mix\ PrOH-hexane}}{{}^{20oC}_{mix\ PrOH-hexane}}$	5319
$Pr' = \frac{{}^{20oC}_{mix\ PrOH-hexane}}{D^{20oC}_{L\,mix\ PrOH-hexane}}$	16.2
$D_L = \frac{110^{-6}}{AB\sqrt{\mu}\left(v_A^{1/3}+v_B^{1/3}\right)^2}\sqrt{\frac{1}{M_A}+\frac{1}{M_B}}$, m^2·s^{-1}	4.8·10^{-8}
$Pe' = RePr'$	86168
$Sh = 0,53Re^{0.54}\left(Pr'\right)^{0.33}$	137
$= \frac{Sh\left(Nu'\right)D}{d_{reactor}}$, s^{-1}	2.1·10^{-4}
$k_L a$, s^{-1}	2.4
$OTR = k_L a\left(C^* - C\right)$, mmol·L^{-1}·h^{-1}	1.5·10^{-3}

Space–time–yield (STY, g·L^{-1} ·h^{-1}) is the key performance indicator for a batch-type catalytic reactor [40]:

$$STY = \frac{[P]f}{R_v} = \frac{3.3410^2\ 0.00053}{0.01} = 0.17710^2 = 17.7\,g\,L^{-1}\,h^{-1},$$

where [P] is the concentration of product leaving the reactor in g·L^{-1}.

As can be seen from the SEM results, the size of the CuNPs supported on SiO$_2$ decreases from 200 to 85,8 μm (Fig. 10). The main changes are size reduction by abrasion and degradation after prolonged agitation [41]. By reducing the particle size of a catalyst, its surface area increases and the reaction rate in the three-phase system is faster.

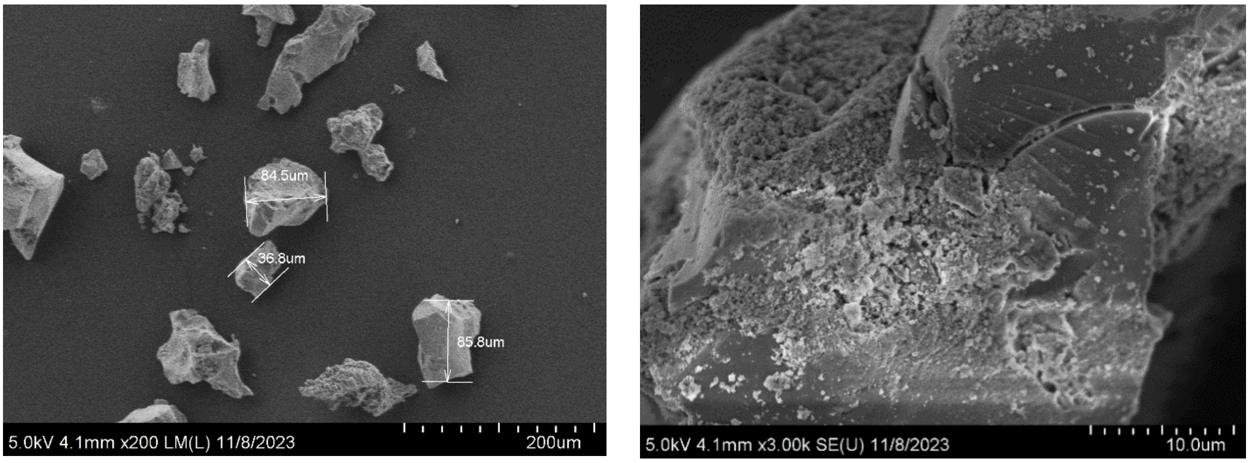


Figure 10. SEM micrographs of CuNPs supported on SiO$_2$ after 9 hours of oxidation process

Oxygen molecules adsorb and dissociate on the Cu(111),(220) surfaces to form an initial layer of atomic oxygen [42]. XRD data indicate the interaction between copper(111),(220) and dioxygen. Atomically adsorbed oxygen oxidizes 1-propanol on the Cu(111),(220) surface forming propionaldehyde and water. 1-Propanol reacts with the decomposed oxygen atoms on the Cu(111),(220) surfaces, forming water as following:

$$C_2H_5CH_2OH + 2O + Cu(111),(220) \rightarrow C_2H_5CHO + H_2O + O + Cu(111),(220). \quad (5)$$

Conclusions

The ratio of PVA to bivalent copper ions was determined to be equimolar by the conductimetric titration. The formation of the PVA-Cu(II) complex was confirmed by UV-Vis and FTIR spectral methods. Copper nanoparticles stabilized by PVA were impregnated on the surface of SiO_2 using a “one-pot” method. The morphology of the nanoparticles was identified by SEM and XRD, demonstrating an amorphous structure. The average size of CuNPs stabilized by PVP varied from 10 to 25 nm. Preliminary experiments indicate that the Cu powder derived from PVA-CuNPs acts as a catalytic precursor for the oxidation of 1-propanol. The oxidation of 1-propanol with oxygen in the presence of a copper catalyst leads to the formation of the key product — propionaldehyde, with yields ranging from 61.4 % to 87.8 % and depending on the mass of catalyst and the process duration. It was shown that a batch-type laboratory catalytic reactor with a total volume of 150 mL can serve as a three-phase (gas-liquid-solid) stirred laboratory tank reactor and evaluated by following different parameters (Re, Pr’, Sh, $k_L a$, STY).

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. CRediT: **Kuralay Sakenkyzy Maksotova** — methodology, investigation; **Dina Nauryzbaevna Akbayeva** — conceptualization, methodology, validation, visualization, original draft preparation, writing-review & editing, supervision, funding acquisition; **Botagoz Sanatkyzy Bakirova** — methodology, validation, investigation; **Akerke Serikkyzy** — methodology, validation, investigation; **Bexultan Mekenbayuly Lesbek** — methodology, validation, investigation; **Gulnur Sairanovna Tatykhanova** — methodology, validation, investigation, supervision; **Sarkyt Elekenovich Kudaibergenov** — conceptualization; methodology, validation, investigation, supervision, funding acquisition.

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Conflicts of Interest

The authors declare no conflict of interest.

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