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***Dedicated to Professor Mircea Diudea
on the Occasion of His 65th Anniversary***

CATALYTIC REDUCTION OF 4-NITROPHENOL USING NEW Cu(0)/AROMATIC CORE DENDRIMER COMPLEXES

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ABSTRACT. Dendrimers are macromolecules with well-defined shape and size, being typically symmetric around the core. A new class of aromatic core 0 generation dendrimers and their Cu(0) complexes were synthetized.

The obtained adducts were tested as catalysts for reduction of 4-nitrophenol. Higher catalytic activity was observed in each case compared to Cu(0) prepared in situ.

Keywords: *dendrimer complexes, aromatic core, catalyst, Cu(0), p-nitrophenol*

INTRODUCTION

Dendrimers chemistry began in 1978 with the synthesis of highly branched macromolecules [1] followed by the synthesis of the first PAMAM dendrimer reported in 1985 by Tomalia's group [2]. Due to their symmetrical shape and controlled size, dendrimers are excellent candidates for dendrimer-based nanocatalysts by binding metal nanoparticles, which leads to mono or bimetallic complexes. It has been reported that bimetallic Cu(II) and Pd(II) complexes with nitrile group derivatized dendrimers show high catalytic activity in case of oxidation reactions [3]; poly(amidoamine) and polypropylene imine (PPI) dendrimer–Pd complexes proved to be suitable for selective hydrogenation [3]. Metal nanocatalysts are also widely used in different oxidation [4], reduction [5] or dehydrogenation reactions [6].

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Phenols and nitrophenol derivatives represent an important class of organic pollutants found mostly in industrial wastewater among dyes. It is well-known that a high number or aromatic contaminants have proven to be carcinogenic and mutagenic in nature [7]. PNP (*p*-nitrophenol) is a frequent byproduct from the pesticides production. Also, it results from pharmaceutical and petrochemical industries. The processes focused on nitrophenol degradation include catalysis among chemical- and photochemical oxidation or biological degradation, respectively [8].

Catalytic reduction of *p*-nitrophenol to *p*-aminophenol (PAP) using $NaBH_4$ as reducing agent in presence of Cu(0) nanoparticles became a model reaction due to the low cost of the catalyst [9]. Literature data reveals also the use of Pt, Au [10], Pd [11] and Ag [12] noble metal nanoparticles in the catalytic reduction process. In order to improve the catalytic activity thus to decrease the reaction time required for the transformation of the PNP, the copper nanoparticles are deposited on different surfaces like porous silicon powder [13], silicon nanowires [14] or mesoporous silica [15] and used in heterogeneous catalysis.

Herein is presented an alternative method for homogenous catalysis using new aromatic core zero generation dendrimers as support for the metallic copper nanoparticles.

RESULTS AND DISCUSSION

For the catalytic activity test of the obtained *2a-Cu, 2b-Cu, 2c-Cu, 2d-Cu* complexes, two aqueous solutions: 1.2 mM PNP and 15 mM $NaBH_4$ were prepared. As a reference, the absorbance spectra of the *p*-nitrophenol was recorded. This revealed a maximum at 318 nm. When PNP was mixed with the reducing agent ($NaBH_4$), the absorbance maximum was red shifted to 401 nm (Figure 1). PAP reveals an absorbance maximum at 300 nm.

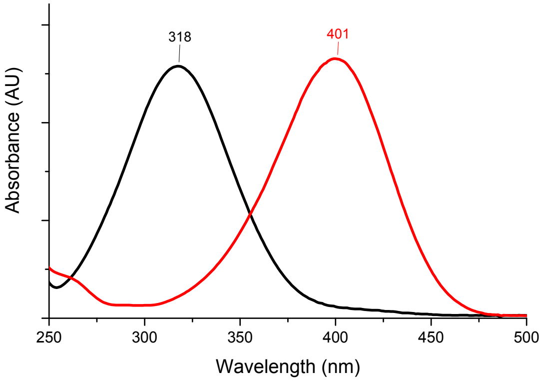


Figure 1. Absorbance spectra of PNP (black trace), PNP+$NaBH_4$ (red trace)

In order to calculate the molar extinction coefficient (ε) by Lambert-Beer law (A= ε·c·l), the absorbance at 401 nm of known PNP concentration solutions was measured. In all cases, the samples contain 1 mL 15 mM $NaBH_4$. The final volume of each sample was 2.7 mL, the cuvette diameter was 1 cm. Figure 2 presents the obtained standard calibration curve. The value of the molar extinction coefficient was determined from the fitted linear equation as being 17.214 L·mmol^{-1}·cm^{-1}. The appearance of the prepared catalysts is shown in Figure 3.

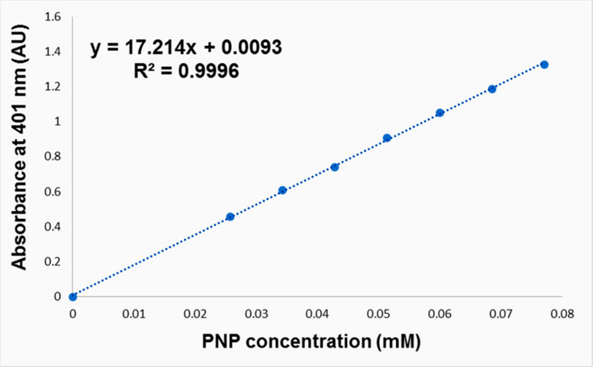


Figure 2. Determination of the molar extinction coefficient

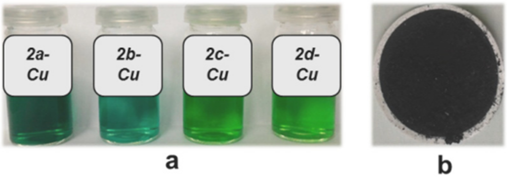


Figure 3. Appearance of the prepared catalysts

When catalyst is added to the PNP+$NaBH_4$ mixture, the reduction of the nitro compound is produced. To each sample containing 180 μL 1.2 mM PNP + 1 mL 15 mM $NaBH_4$ and 1.62 mL DI H_2O, 30 μL of catalyst (*2a-Cu, 2b-Cu, 2c-Cu, and 2d-Cu*) was added. As a reference, Cu(0) was used (1 mg). The kinetic data acquisition was performed for 500 s in each case and spectra were recorded at 0.5 s intervals at room temperature under continuous stirring (480 rpm) at two fixed wavelengths 300 and 401 nm, for monitoring the PNP consumption (401 nm) and the PAP formation (300 nm), respectively.

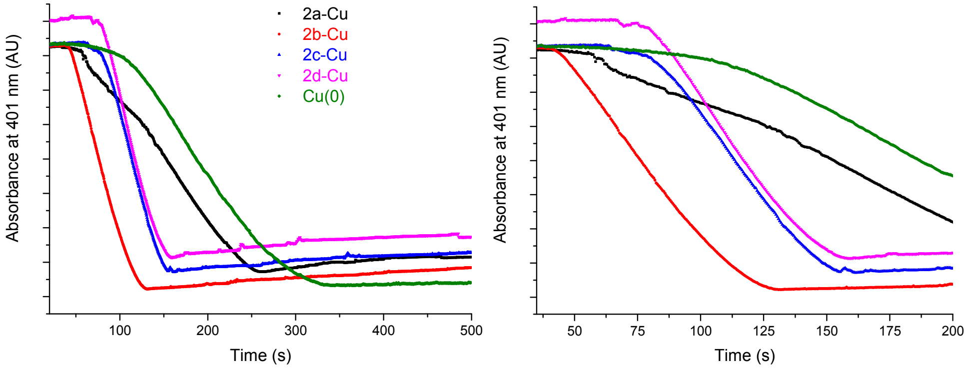


Figure 4. Monitoring the catalytic reaction in time

Experimental data show that each catalyst (*2a-Cu, 2b-Cu, 2c-Cu, 2d-Cu*) shows a higher activity compared to the reference Cu(0). Within this, the hydrogenation reaction was the fastest when *2b-Cu* catalyst was used (Figure 4). As can be seen in Figure 5, the characteristic peak for PNP (black trace) disappeared (by the catalyst addition to the PNP+$NaBH_4$ mixture) after 65 s and the peak for PAP appeared at 300 nm wavelength (red trace) proving the transformation of the nitro compound.

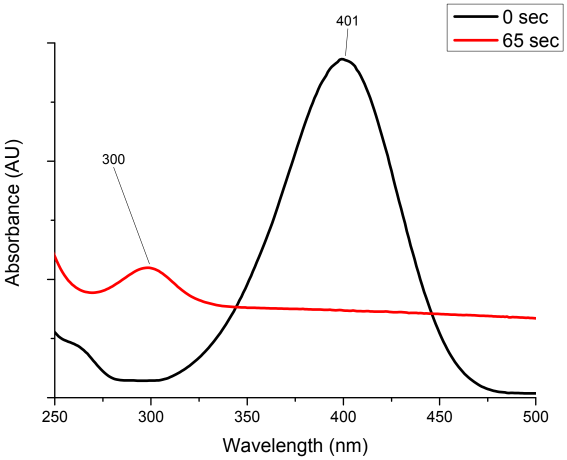


Figure 5. Reaction monitoring using *2b-Cu* catalyst

The reaction rate was assumed to be independent of the $NaBH_4$ concentration in all cases, therefore pseudo first order kinetic equation was applied when *2b-Cu* was used as catalyst (Figure 6).

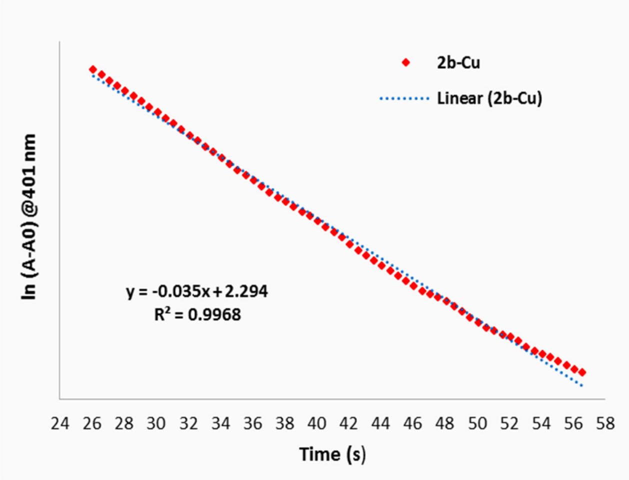


Figure 6. Pseudo first order kinetic plot of PNP reduction catalyzed by *2b-Cu*

CONCLUSIONS

The use of Cu(0)/dendrimer complexes as catalysts in the homogenous chemical reduction of PNP represents a good alternative to the heterogeneously catalyzed reduction. The reaction time highly decreased in comparison with Cu(0) nanoparticles prepared in situ used as heterogeneous catalyst.

EXPERIMENTAL SECTION

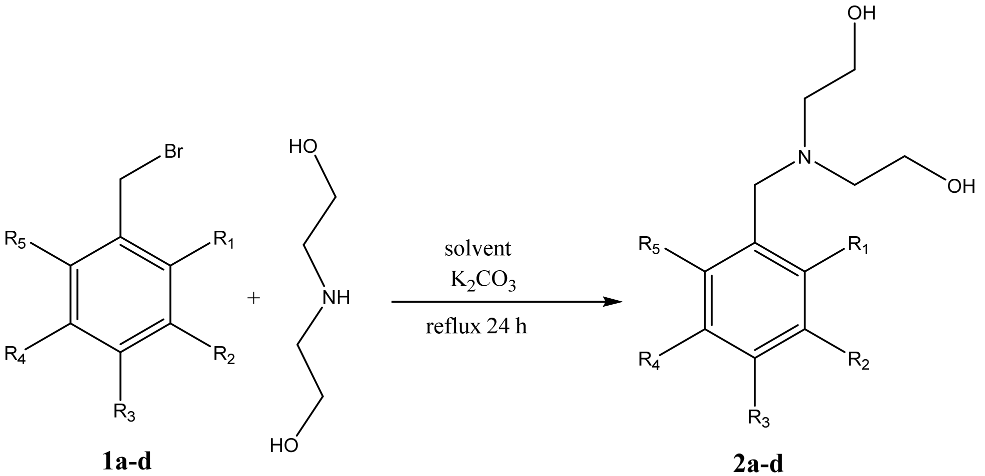
Materials and methods

1,4-bis(bromomethyl)benzene, copper(II) chloride dihydrate, 1,3,5-tris(bromomethyl)benzene, 1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene, anhydrous potassium carbonate, 1,2,4,5-tetrakis(bromomethyl)benzene, 4-nitrophenol and diethanolamine were purchased from Sigma-Aldrich. The solvents were supplied from Merck. All reagents were used as received without further purification.

Thin layer chromatography (TLC) monitoring was carried out using Merck Kieselgel 60 F 254 sheets. Spots were visualized under UV light at 254 nm. UV-Visible absorbance spectra were recorded on Agilent 8453 spectrophotometer. Mass spectra of the dendrimers were recorded on Agilent /Technologies 6320 spectrometer at room temperature while their ^{1}H and ^{13}C NMR spectra were recorded on Bruker spectrometers operating at 400 and 100 MHz respectively at 600 and 150 MHz.

Synthesis of dendrimers

In the first step, the dendrimers were prepared according to the procedure previously described by [16]. For the preparation of a novel zero generation dendrimer (compound *2d*), a tetrasubstituted benzene core, namely 1,2,4,5-tetrakis(bromomethyl)benzene was used. The synthesis was carried out under similar conditions using a mixture of solvents instead of MeCN (dioxane:acetonitrile 2:1). The general procedure is presented in Scheme 1.



1a-d

2a-d

1a: R_1, R_2, R_4, R_5 : -H
R_3 : $-CH_2-Br$
1b: R_1, R_3, R_5 : -H
R_2, R_4 : $-CH_2-Br$
1c: R_1, R_3, R_5 : $-CH_3$
R_2, R_4 : $-CH_2-Br$
1d: R_2, R_5 : -H
R_1, R_3, R_4 : $-CH_2-Br$

2a: R_1, R_2, R_4, R_5 : -H
R_3 : $-CH_2-N-(CH_2-CH_2-OH)_2$
2b: R_1, R_3, R_5 : -H
R_2, R_4 : $-CH_2-N-(CH_2-CH_2-OH)_2$
2c: R_1, R_3, R_5 : $-CH_3$
R_2, R_4 : $-CH_2-N-(CH_2-CH_2-OH)_2$
2d: R_2, R_5 : -H
R_1, R_3, R_4 : $-CH_2-N-(CH_2-CH_2-OH)_2$

Scheme 1. General procedure for the synthesis of dendrimers

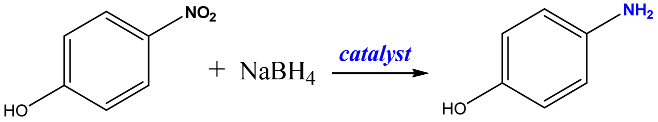
Preparation of catalysts

A solution of 5 % $CuCl_2 \cdot 2H_2O$ in methanol was prepared. In a 10 mL round bottom flask to 5 mL of copper salt solution 0.18 mmol dendrimer ***2a-d*** dissolved in 1 mL MeOH was added dropwise under continuous stirring. The resulted mixture was refluxed for 24 h, let to reach room temperature, filtered and washed with MeOH (5 mL). To the filtrate 1.85 mmol $NaBH_4$ was added portionwise under strong stirring for the reduction of the Cu^{2+} to metallic copper. The resulted suspension was filtrated on PTFE membrane filter (0.22 μm pore diameter) under vacuum in order to remove the formed solid Cu(0) nanoparticles which were not encapsulated into the dendrimer's cavity. The precipitate was washed with MeOH (5 mL). The resulted filtrate (Figure 3a) was used as catalyst (noted further as *2a-Cu, 2b-Cu, 2c-Cu, 2d-Cu*) and its activity was tested within the chosen model hydrogenation reaction[9] (Scheme 2).

As the reference, Cu(0) was prepared as follows: in an Erlenmeyer flask, at 5 mL of the prepared copper(II) chloride dihydrate methanolic solution, 70 mg $NaBH_4$ was added portionwise under rigorous stirring. The resulted solid metallic copper nanoparticles (Figure 3b) were filtered off on PTFE membrane filter (0.22 μm pore diameter) and dried in air.

Catalytic activity testing

For the catalytic activity testing of the dendrimer-Cu(0) complexes the reaction presented in Scheme 2 was followed.



Scheme 2. Reduction of *p*-nitrophenol

The reaction was monitored spectrophotometrically. The yellow colored *p*-nitrophenol aqueous solution turned into colorless and contained black solid particles. This proved, that upon the catalysis Cu(0) nanoparticles bounded into the dendrimers were released.

ACKNOWLEDGMENTS

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