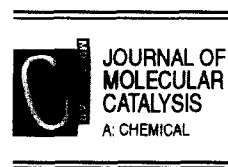




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Catalytic oxidation and photo-oxidation of nitrophenols by strong oxidants generated in situ via CuO-aerogel

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Abstract

Nitrophenols have been catalytically degraded with high efficiency by a novel CuO-aerogel powder with a surface area (20 m²/g) having a high Cu(I) content. The reaction proceeds in acid media (room temperature) thermally and more efficiently under visible light and O₂(air).

Keywords: Nitrophenol catalytic degradation; Photocatalysis; CuO-aerogel; Cyclic; Voltammetry; XPS

1. Introduction

Up to now, direct photolysis has not been found effective in processes involving nitrophenols degradation [1,2]. However, heterogeneous catalytic systems using TiO₂ slurries [3] and zeolites [4] have been relatively successful for this purpose. Also homogeneous Fenton reactions [5,6] have been reported to be useful in this context. Thus, in line with our efforts to find new methods for the abatement of these non-biodegradable pollutants [7] we tried a new copper oxide catalyst under the form of a CuO-aerogel. Such an aerogel should present a large surface area and possibly the number and variety of copper species activating the desired catalysis.

2. Experimental

Cu(II)O, Cu(I)₂O, 2-nitrophenol, 2,4 and 2,5-dinitrophenols were Fluka reagents and were used as received. The CuO-aerogel was synthesized using the sol-gel method [8,9] involving the hydrolysis of a mixture of Cu(II) acetate (monohydrated) diluted in 50% acetone in water containing a few drops of ammonia as catalyst. The resulting mixture was placed in an autoclave with 450 ml of methanol and supercritically dried at 250°C. A very fine powder was obtained exhibiting a specific surface area of 20 m²/g.

Photolysis experiments were carried out by means of a Hanau Suntest Lamp (AM 1). The radiation flux entering the photolysis flask was 90 mW/cm². Photolysis was carried out in 60 ml Pyrex flasks using 40 ml solutions. Acidification of the samples was carried out with 0.1N

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HCl. The CuO powders were centrifuged out of the solution at 10,000 rpm for 30 min and subsequently washed several times with water. The solutions used to carry out dissolved organic carbon (DOC) determination or high pressure liquid chromatography (HPLC), were filtered through a 0.1 μ Millipore filter before analysis. The copper in solution has been assessed via the neo-cuproin reagent [10] following the absorption of the Cu-neocuproin complex in chloroform solution. The absorbance at $\lambda = 457$ nm was measured against appropriate blanks. This analysis was capable of determining the total amount of Cu in the solution down to 1 ppm. To identify specifically the Cu⁺¹-ion present we added Fe⁺³-ions (1 mM) at pH 2.5. The Cu⁺¹ reacts with Fe⁺³ and the resulting Fe⁺² complexes with o-phenanthroline. The Fe-phenanthroline complex showed a peak at $\lambda = 510$ ($\epsilon = 1.2 \cdot 10^4$ M⁻¹ cm⁻¹).

High pressure liquid chromatography (HPLC) was carried out via a Varian 5500 unit. A spherisorb silica column with a methanol water gradient elution was used. Optical signals were detected at $\lambda = 315$ nm. Dissolved organic carbon (DOC) was monitored via a Shimadzu 500 instrument. The CO₂ evolved during the degradation was followed by gas chromatography (GC) Carlo Erba 2000 provided with a Poropak Q column. Cyclic voltammetry was carried out via Wescan potentiostat (for other details see text below). Photoelectron Spectroscopy (XPS) was carried out using a Leybold-Heraeus instrument and Mg K α 1,2 line at 1253.6 eV. The quantitative evaluation of the data used a poly-

nomial fit (Shirley type) with background subtraction. Binding energies were referenced to the Au 4f_{7/2} gold doublet at 83.8 eV.

3. Results and discussion

XPS runs were performed on the CuO-aerogel surface and revealed three species Cu(I), Cu(II), Cu(O) in the corresponding percentages of 80, 15 and 5%. By comparison a commercial Fluka CuO analyzed by XPS in the same way exhibited a composition of Cu(I), Cu(II), Cu(O) very different from our catalyst, since it was observed in percentages: 5, 90 and 5 respectively. The latter material had also exhibited a surface area of 2 m²/g.

Table 1 presents the degradation results for 2-nitrophenol using different Cu-oxide catalysts. Experimental data for the half-time of degradation (HPLC), residual carbon after 25 h (DOC) and CO₂ evolved in the dark and under light. Results are shown for the different oxides used with their different catalytic behaviour towards the degradation of the substrate.

Fig. 1 presents the results for the dark and photodegradation of a solution containing 2-nitrophenol ($0.8 \cdot 10^{-3}$ M) and 1 g/l CuO-aerogel. Up to six consecutive degradation cycles of 2-nitrophenol were tried to test the long term performance of the catalyst. After each reaction that lasted 24 h fresh nitrophenol was added after washing the mediator with water before reuse. From Fig. 1 it was seen that CuO can be reused over many cycles. Little decrease

Table 1
2-Nitrophenol (0.8×10^{-3} M) = A; Cu-Oxide (1 g/l); pH 2.5 (if not included)

	A, dark, $t_{1/2}$	A, light, $t_{1/2}$	A, dark, left%, 25 h	A, light, left%, 25 h	DOC, dark, left%, 25 h	DOC, light, left%, 25 h	pH 4, dark, $t_{1/2}$	pH 4, light, $t_{1/2}$	% stoichio. CO ₂ , dark, 25 h	% stoichio. CO ₂ , light, 25 h
CuO aerogel	3/4 h	1/2h	11	3	19	13	35 h	25 h	4	12
Cu(I) fluka	1 h	3/4 h	17	33	23	20	40 h	35 h	2	6
CuCl fluka	4 h	2 h	67	50	45	35	—	—	—	—
Cu(II)O fluka	> 60 h	> 50 h	80	70	58	50	—	—	—	—

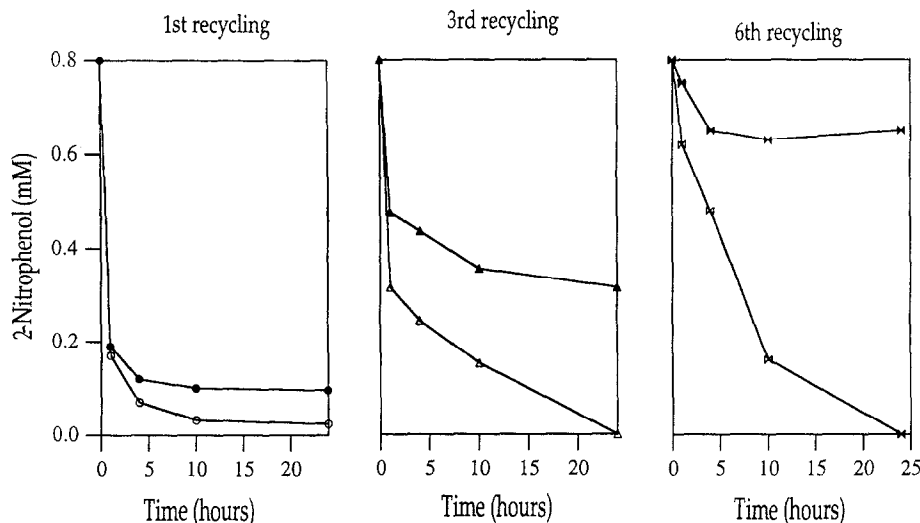


Fig. 1. Catalytic degradation of 2-nitrophenol (0.8×10^{-3} M) on CuO-aerogel (1 g/l) under light irradiation via a solar simulator (open points) and in thermal reactions (dark points).

was observed in the activity of the CuO-aerogel even at relatively long reaction times involving many cycles. After a 24 h reaction, a small decrease in the initial rate seems to take place due to the well known lowering of the dispersion of the active species at the catalyst surface during consecutive cycles. In the dark, the degradation of 2-nitrophenol was observed to be less efficient. Hydroxylic sites on the CuO sur-

face are suggested to be involved in the degradation process [1,8,9]. About $4 \cdot 10^{14}$ hydroxylic sites/cm² could be estimated [9] for the CuO aerogel.

Fig. 2 presents the copper dissolved during thermal and light experiments for the first and third run for a solution with the same make up as the one used in Fig. 1. The soluble copper in solution has been determined via the 'neo-

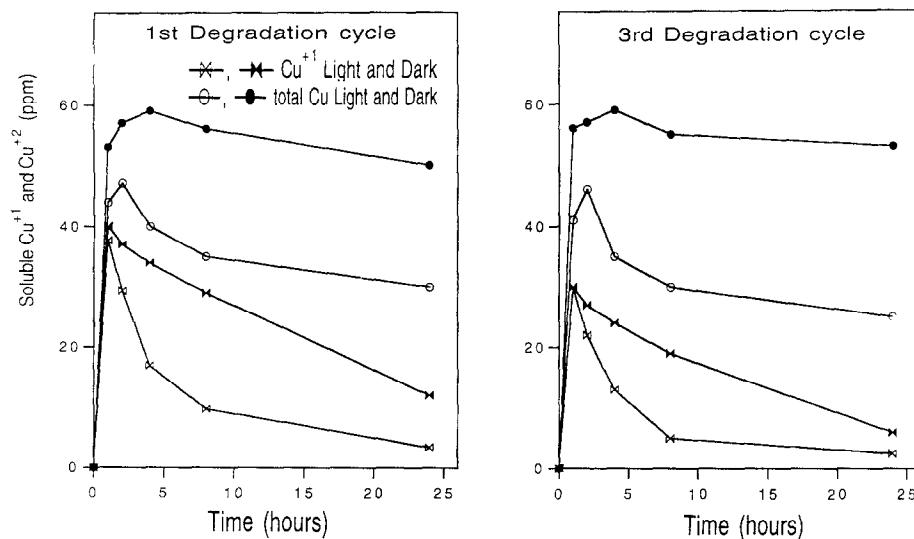
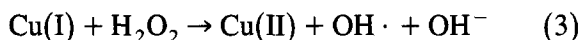
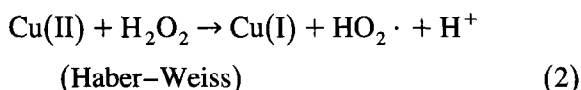
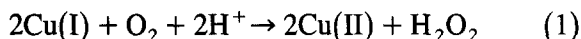


Fig. 2. Copper in solution during degradation in thermal and light induced reactions as a function of time. Captions to the solutions used noted inside the figure. Solutions with the same make-up as in Fig. 1.

cuproin' reagent as mentioned in the experimental part. It is readily seen that the total copper in the solution decreases more steeply for irradiated solutions than for the thermal reactions. This effect is more pronounced for Cu^{+1} -ion (in the dark or under light). This is the species mainly responsible for the observed degradation and recycling of the Cu-species in Fig. 2.

Earlier work reported by the Haber–Weiss cycle [11] involved the recycling of the couple $\text{Fe}^{+2}/\text{Fe}^{+3}$ intervening favourably in catalytic reactions. This system has been widely used to degrade many aromatic compounds in solution [1,5,6] in thermal or light induced reactions. During our studies it was found that Cu(II) ions added homogeneously to a solution of 2-nitrophenol at pH 2.5 in the dark or under light did not induce 2-nitrophenol degradation. The possible Cu(I) intervention in the matrix of the CuO -aerogel is suggested below:



When additional H_2O_2 is added during the degradation it accelerated this process indicating the favourable intervention of $\cdot\text{OH}$ radicals in

these reactions. The H_2O_2 as such could not be analysed since this substance decomposes in the presence of Cu(I) [13]. No metallic copper was observed during 2-nitrophenol degradation. The results (Fig. 2) could be explained by the assumption that Cu(I) was reoxidized to Cu(II) by the oxygen present (air) as shown in Eqs. (1)–(3). Oxygen purging accelerated the photodegradation of 2-nitrophenol by 50% (respect to air) while Ar decreased drastically the photo-oxidation kinetics.

In spite of the common assumption that Fenton reagent produces free $\cdot\text{OH}$ radicals, the formation in our case of a highly stabilized six member complex between Cu^{+1} and 2-nitrophenol could generate a nucleophilic adduct (Cu^{+2} -nitrophenol-OOH). This species may also be the dominant reactive intermediate during the degradation [12]. Fenton-like reagents forming electrophilic transition-metal complexes (Fe^{+2} or Cu^{+1} as shown in Fig. 2) have been reported in nucleophilic addition to metal centers in mechanisms free of $\cdot\text{OH}$ radicals [13].

To assess the electron donating capacity of 2-nitrophenol cyclic voltammetry was carried out and the results presented in Fig. 3. The oxidation potential was measured using Ag/AgCl in saturated KCl at pH 7. Fig. 3a shows a potential of 0.96 V as indicative for the

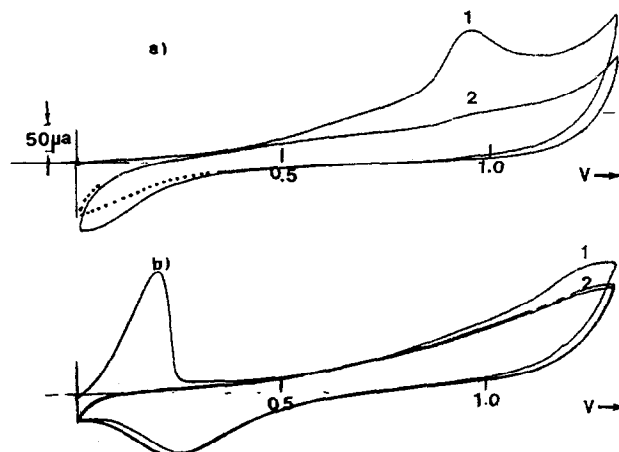
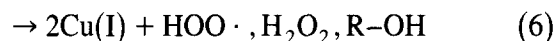
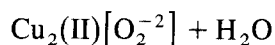
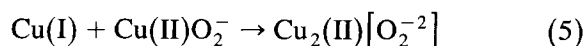
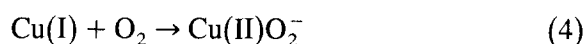


Fig. 3. (a) Cyclic voltammograms of a solution 0.8×10^{-3} M 2-nitrophenol at pH 7 and Pt-electrode. (b) The same solution containing 2-nitrophenol, CuO -aerogel at pH 2.5. For other details see text.

oxidation potential of 2-nitrophenol. Since the second cycling is different from the first a film of the substrate forms on Pt. This 2-nitrophenol film cannot be recycled. When CuO-aerogel is added at pH 7, the cyclic voltammograms are identical to the ones reported in Fig. 3a. Fig. 3b reports on the reaction taking place when CuO-aerogel and 2-nitrophenol at pH 2.5. A half wave oxidation potential of 1.2 V versus NHE was found during the first recycling. The peak of the $\text{Cu}^+/\text{Cu}^{+2}$ couple is then seen by 0.23 V versus NHE. This latter value for the oxidation-reduction potential of $\text{Cu}^+/\text{Cu}^{+2}$ on the CuO-aerogel matrix is seen to be different by 0.16 V from the standard value in solution [14]. This latter potential varied in the voltammograms according to the concentration of the catalyst, 2-nitrophenol and gas atmosphere used. As detected by XPS, the Cu(I)/Cu(II) existing on the catalyst surface would participate in the redox reactions taking place. The catalyst allows these Cu-ions during the reaction to enter the solution. During more than 10 consecutive degradations, similar results to the ones reported in Fig. 2 were observed revealing the stable nature of the catalyst used. Cu(II) probably scavenges a significant portion of HO_2/O_2^- leading to the appearance of Cu(I) [15,16] (see Eqs. (4)–(7) below). The second recycling in Fig. 3 indicates non reversibility for the oxidation of the substrate.

It is suggested that Cu(I)-ions adsorbed on the CuO aerogel may be the active degradation species under light or in dark reactions. The reactions would be heterogeneous–homogeneous in nature. It was observed that Cu(I)-ions added homogeneously in solution (from chlorides or nitrates) did not induce 2-nitrophenol degradation either under light or in dark reactions. In fact Cu(I) irreversibly reacts with O_2 [15,16]

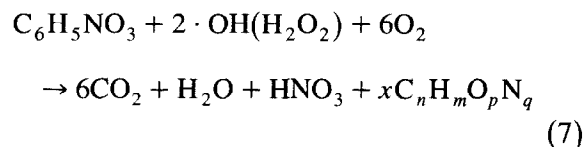


and it has been reported that Cu(I) interacts strongly forming complexes with N-containing groups.

Other Cu-oxides than the aerogel were also tried but they were not effective in catalyzing 2-nitrophenol photodegradation like Cu(I)O Fluka having (1–2 m^2/g) and showing 15% Cu(I) by XPS measurements. This lends further support for Cu(I) containing materials with a relative large B.E.T. surface area as being essential for efficient catalytic action. In addition, the amount of photodegradation observed with 2,4 dinitrophenol and 2,5 dinitrophenol was about 50% of the one observed for the mono-substituted phenols over a 24 h period. The fact that degradation was possible even if it was not complete in the case of dinitrophenols is important because biodegradation of dinitrophenols by sewage bacteria or activated sludge does not proceed at all [7]. This is due to the toxicity of the intermediates generated during the biological degradation process.

The percentage of phenol left after 8 h in the Dark (*D*) and under light (*L*) is shown in Table 2 when CuO-aerogel is compared with other well known oxidants: H_2O_2 (5×10^{-3} M), KMnO_4 (2×10^{-3} M) and $\text{K}_2\text{Cr}_2\text{O}_7$ (2×10^{-3} M) for the oxidation of 2-nitrophenol. CuO-aerogel revealed itself to be more efficient than the other strong oxidants listed above.

The overall oxidation and photo-oxidation of 2-nitrophenol could be described as:



The structure of $x\text{C}_n\text{H}_m\text{O}_p\text{N}_q$ is being determined presently in our laboratory.

The abatement of nitrophenols via novel Cu-oxides in heterogeneous systems has been shown to proceed in a catalytic fashion. The levels of Cu generated in the solution during the photo-

Table 2
Oxidation efficiencies towards 2-nitrophenol^a

2-Nitrophenol	H ₂ O ₂		KmnO ₄		K ₂ Cr ₂ O ₇		CuO					
	HPLC	DOC	HPLC	DOC	HPLC	DOC	HPLC	DOC				
	D	L	D	L	D	L	D	L				
85	36	96	94	94	92	94	97	98	31	12	35	22

^a HPLC: High Pressure Liquid Chromatography; DOC; Dissolved Organic Carbon.

oxidation do not attain levels that may affect adversely bacterial strains adapted for Cu elimination.

4. Conclusions

The photooxidation of nitrophenols has been reported here via novel copper oxides with a large surface area. The degradation of nitrophenol was strongly dependent on the preparation and surface characteristics of the Cu-oxide employed in the reaction. Cu-ions added homogeneously in the dark or under light did not induce any degradation in a variety of phenols tried. The oxidation potential of the couple $\text{Cu}^+/\text{Cu}^{+2}$ in the CuO variety used was determined to be different from the values reported in solution under standard conditions. Light induced partial mineralization led to CO_2 , nitrates, nitrites, ammonia hydrogen, and an insoluble polymer.

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