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Efficient catalytic wet peroxide oxidation of phenol at moderate temperature using a high-load supported copper catalyst

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HIGHLIGHTS

- The CuO/γ-Al_2O_3 catalyst gave complete phenol conversion and 85% TOC reduction.
- High peroxide efficiency achieved with concentrations close to stoichiometric.
- Catalyst used in consecutive runs yields similar performance.

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ABSTRACT

The use of hydrogen peroxide as the oxidizing agent in the presence of a catalyst (Catalytic Wet Peroxide Oxidation, CWPO) has emerged as a clean and effective alternative among other catalytic oxidation processes. The objective of this study is to evaluate the CWPO of phenol solutions using a high-load CuO/Al_2O_3 catalyst, which allows maintaining a high activity and efficiency compared to homogeneous copper, also overcoming secondary effluent contamination.

The catalytic oxidation of aqueous phenol solutions using H_2O_2 as oxidizing agent and a home-made CuO/Al_2O_3 catalyst was studied in a batchwise slurry reactor. The applied H_2O_2:phenol molar ratio was only nearly 30% higher than the stoichiometric ratio. Experiments were performed at temperatures between 303 and 343 K using different catalyst loads. Phenol disappearance and TOC reduction were monitored throughout the reaction time.

Both phenol and TOC conversions were larger as temperature and catalyst load increased, following the higher hydrogen peroxide decomposition rates achieved. At the highest catalyst load and temperature, complete phenol conversion and ca. 80% TOC removal was achieved. Catalyst performance in terms of phenol and TOC disappearance was maintained after 12 h of usage. Although there is evidence of some copper leaching from the catalyst, the homogeneous contribution to the overall activity is marginal.

1. Introduction

Phenols frequently appear in wastewater from refineries, petrochemical, pharmaceutical, coal and many other industries [1]. Their removal is still an important area of research as increasingly stricter wastewater discharge standards continue to be worldwide implemented.

Several technologies are useful to eliminate industrial organic wastes based on biological, physical and chemical treatments. Conventional biological processes are not adequate to treat highly non-biodegradable wastewater and usually require too long residence time for micro-organisms to degrade the pollutants, when possible. Physical treatments, which include flocculation, precipitation, adsorption on activated carbon, air stripping or reverse osmosis, are not definitive, requiring a further destructive post-treatment [2]. Therefore, in the last years, different chemical treatment technologies have been developed and are currently considered for industrial application. Among them, Advanced Oxidation Processes (AOPs) comprise a number of different oxidation treatments exploiting the high reactivity of oxyradicals. AOPs include many techniques, including recent methods based on ultrasound plasma and electrohydraulic discharge along with more classical processes based on hydrogen peroxide (H_2O_2/UV, Fenton, photo-Fenton and Fenton-like processes) or ozone [3].

The use of hydrogen peroxide as the oxidizing agent in the presence of a catalyst (Catalytic Wet Peroxide Oxidation, CWPO) has emerged as a clean and effective alternative among other catalytic oxidation processes [4–6]. Hydrogen peroxide does not form any harmful by-products, is a non-toxic reactant, improves the

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oxidation efficiency and tempers the needed reaction conditions ($T < 323$ K, 0.1–0.3 MPa). However, two major drawbacks, i.e. narrow acidic pH range and the need for removing the homogeneous catalyst, must be pointed out. Moreover, poor use of hydrogen peroxide often requires working in high excess of oxidant. The use of heterogeneous catalysts based on low-valence transition metals appears as a promising option to overcome these problems since oxidation efficiencies are relatively high and pH sensitivity is lower compared with homogeneous catalysts at the same operating conditions.

Therefore, a variety of catalysts containing Fe, Cu or other transition metal precursors supported on different materials (oxides, clays, zeolites, natural and synthetic polymers) have been tested in CWPO [7–9]. The reaction mechanisms associated to copper in solution or on a solid catalyst have been presented by several authors [5,7,10–12]. Besides the classic redox cyclic mechanism involving Cu^+ and Cu^{2+}, an additional pathway with formation of a hydroperoxo complex intermediate, which then transforms to cupryl ion generating a hydroxyl radical, is possible. The two pathways are characterized by a different turnover frequency as well as efficiency in H_2O_2 use. Starting from Cu^{2+} (as in Fenton like heterogeneous catalysts), the occurrence of the either pathway depends on the energetic stability of the hydroperoxo complex, which in turn depends on the ligand effect of the substituents [10,11].

Results on phenol CWPO, at atmospheric pressure, in the presence of only copper as active metal, are reviewed in Table 1. Experiments were carried out with different catalysts and under diverse reaction conditions, such as catalyst load, temperature, phenol and H_2O_2 concentrations, reaction time and pH of the reaction media. Although it is not possible to strictly compare catalyst performances, the results indicate that to obtain a high degree of mineralization, more drastic conditions are necessary (higher temperature and/or catalyst load) [13,19,21]. Furthermore, catalyst leaching is reported in almost all studies.

The purpose of this work is to study the catalytic oxidation of phenol solutions with hydrogen peroxide using a home-made CuO/Al_2O_3 catalyst containing high metal load. In previous investigations, this catalyst was able to successfully oxidize phenol in CWAO experiments at 0.8 MPa oxygen pressure and 413 K [22]; however, to the best of our knowledge, there are no references in the literature concerning its use for CWPO.

2. Experimental

2.1. Catalyst preparation

The CuO/Al_2O_3 catalyst was prepared using the molten salt method, as described elsewhere [22,23]. The metallic precursor was $Cu(NO_3)_2{\cdot}2.5H_2O$ (p.a., MERCK); the catalyst support was γ-Al_2O_3 (ALFA AESAR, 1/8″ pellets, BET surface area 214 m^2/g, average pore volume 0.67 cm^3/g). The salt was molten at 423 K, and the alumina was preheated at the same temperature. A muffle furnace with integrated air circulation was used (temperature ramp at 7 K/min). The molten salt and the support were mixed and left in contact for 30 min at 423 K. The resulting preparation was cooled at room temperature for 24 h. Then, the sample was dried in a conventional oven at 383 K (12 h), and calcined at 673 K for 4 h under air flow (10 ml/min).

2.2. Catalyst characterization

The copper content of fresh and used samples was determined by soaking the catalyst in 65% HNO_3 solution and then analyzing the copper concentration using Atomic Absorption Spectroscopy (AAS) in an ANALYST 300 Perkin-Elmer Spectrophotometer. Copper leached from the catalyst during operation was also measured by AAS.

Table 1
Phenol CWPO, under atmospheric pressure with only copper as active metal.

Catalyst	Phenol conversion (%)	TOC conversion (%)	pH	Conditions	Leaching (%)	Ref.
CuO impregnated activated carbon	100% Phenol	68% TOC Adsorption values around 30%	Not controlled	Phenol 1 g/l, H_2O_2 0.1 mol/l, 2 g/l catalyst, 180 min, 80 °C, 4,6–38.9 wt.% of active metal	Not reported	[13]
Cu/ZSM-5 by hydrothermal synthesis	Phenol 36, 68, 85, 92% (50, 60, 70, 80 °C)	TOC results are not reported	Not controlled	Phenol 0.01 mol/l, H_2O_2 0.1 mol/l, catalyst 0.1 g/l,180 min, 50–80 °C, 1.62 wt.% of active metal	3.20%	[14]
Cu/ZSM-5 by ion-exchanged synthesis	Phenol 20, 56, 81, 96% (50, 60, 70, 80 °C)	TOC results are not reported	Not controlled	Phenol 0.01 mol/l, H_2O_2 0.1 mol/l, catalyst 0.1 g/l, 180 min, 50–80 °C, 2.53 wt.% of active metal	4.80%	[14]
Cu/α-Al_2O_3	100% Phenol	48% TOC adsorption values nor thermal decomposition were reported at 90 °C	Not controlled	Phenol 0.01 mol/l, H_2O_2 0.1 mol/l, catalyst 5 g/l, 180 min, 90 °C, 1 atm, 1 wt.% active metal	65%	[15]
Cu–Y-5	Phenol 50, 70, 80, 80% (50, 60, 70 and 80 °C)	TOC results are not reported	Not controlled	Phenol 0.01 mol/l, H_2O_2 0.03 mol/l, catalyst 0.1 g/l, 180 min, 50, 60, 70 and 80 °C, pH 3,5–4, 4.09 wt.% of active metal	4.80%	[6]
Polymer-supported copper complexes: polybenzimidazole loaded with copper	72% Phenol	54% TOC adsorption 15.8%	Buffered pH 6	Phenol 1 g/l, Phenol/H_2O_2 molar ratio of 1:14, 50 mg/l Cu^{2+}, 240 min, 40 °C	6%	[16]
Al–Cu modified clays	Not reported	Approx. 60% TOC	pH 4–5	Phenol 0.0005 M, H_2O_2 5 ml 0.5 o 0.1 N, catalyst 0.5 g, Cu 0.16–0.39%, 20 h, 20 °C	2.5 ppm	[17]
Pillared clays containing copper	30% Phenol	21% TOC	pH 5,5 adjusted to the required value with a dosimeter	Phenol 0.0005 M, H_2O_2 5 ml 0.5 o 0.1 N or 2 ml/h 0.1 N, catalyst 0.1–1 g, CAZA (Cu) 0.67%, 240 min, 20 °C	0.45%	[18]
Cu/13X zeolite	100% Phenol	50–55% TOC	Not controlled	Phenol 0.01 mol/l, H_2O_2 0.1 mol/l, catalyst 0.5 g/l,180 min, 60–80 °C, 3.4–3.7 wt.% of active metal	20%	[19]
Cu-silicate-1	49.2% Phenol	TOC results are not reported	Not controlled	Phenol 1 g/l, H_2O_2 0.1 mol/l, catalyst 0.6 g/l, 120 min, 70 °C, 0.38 wt.% of active metal	63.5%	[20]
BASF Cu-0226 S	100% Phenol	76% TOC (70 °C)	Not controlled	Phenol 1 g/l, H_2O_2 0.19 mol/l in one dose or two doses; catalyst 1 or 25 g/l, 180 min, 25–70 °C, 12.5 wt.% of active metal	0.60%	[21]