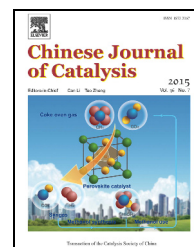


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Article

Simultaneous removal of nitrobenzene and phenol by homogenous catalytic wet air oxidation

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ABSTRACT

The simultaneous wet air oxidation of nitrobenzene (NB) and phenol with homogenous catalyst was carried out in a stainless autoclave in a temperature range of 150–210 °C and at a partial oxygen pressure of 1.0 MPa. Compared with the non-catalytic co-oxidation of NB and phenol, the presence of the homogeneous catalyst greatly improved the conversion of both compounds. The transition metal ions Cu²⁺, Co²⁺ and Ni²⁺ were found to be effective catalysts, with Cu²⁺ affording the best results. How phenol was added to the autoclave was investigated and was found to affect the conversion of NB. Adding phenol in smaller portions can help to degrade NB more effectively. As an example, two additions of phenol with Cu²⁺ as the homogenous catalyst allowed 95% conversion of NB at 200 °C in 1 h. This catalytic co-oxidation method incorporating the addition of phenol initiator batches therefore provides an alternative and effective means of removing persistent organic pollutants from the environment.

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1. Introduction

Nitrobenzene (NB) is widely used in the manufacture of different types of industrial products such as dyes, explosives and pesticides. It has also been used as a solvent to make paint, shoes and polishes [1,2]. NB may be released into the environment during its varied uses and, because of its mutagenicity, environmental persistence and tendency to bioaccumulate, NB is listed as one of the priority organic pollutants by the United States Environmental Protection Agency (http://iaspub.epa.gov/waters10/rpt_epa_num_criteria.run_report).

The direct oxidation of NB can be very difficult because of the low electron density around its benzene ring [3]. During the last two decades, a number of advanced oxidation processes

(AOPs), such as photo-catalytic oxidation [4], ozonation [5], Fenton oxidation [6] and combined oxidation [7,8], have been applied to the degradation of NB. Among these, wet air oxidation (WAO), initially proposed and developed by Zimmermann, appears to show particular potential with regard to wastewater treatment. Unlike other AOPs, WAO is an attractive method for the treatment of waste streams with chemical oxygen demand from 10–100 g/L that are too dilute to incinerate but too concentrated for biological treatment [9]. During WAO, the waste is oxidized into carbon dioxide, water and low molecular weight organic acids at elevated temperatures (150–325 °C) and pressures (0.5–20 MPa) using pure oxygen or air as the oxidant [10,11]. WAO is not only eco-friendly but also more economical compared with other AOPs that often use harmful

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and/or expensive oxidizing agents, such as ozone and hydrogen peroxide. To achieve the oxidation of pollutants under milder conditions, catalytic wet air oxidation (CWAO) processes have been developed since the 1970s, especially for wastewater treatment [12–14].

In recent years, co-oxidation methods have been increasingly employed to further improve the oxidation efficiency of WAO processes. Willms et al. [15] first observed that the efficiency of *m*-xylene oxidation increased with the introduction of the more easily oxidizable phenol to the reaction system. Similar results have been reported in which the addition of cellobiose or phenol to solutions containing recalcitrant low molecular weight acids led to enhanced oxidation rates [16]. The degradation rate of thiocyanate was also significantly enhanced when it was simultaneously oxidized with cyanide under the same conditions [17]. We also reported that the presence of phenol in the reaction media greatly improves the conversion of NB [18,19], and that the simultaneous degradation of trichlorophenol and nitrophenol is possible by wet air co-oxidation [20]. Although co-oxidation of pollutants has been previously reported, there has been little investigation of co-oxidation in the presence of catalysts.

Herein we report the first-ever catalytic co-oxidation of NB and phenol using homogenous catalysts. Homogeneous catalytic oxidation was chosen because of its simplicity and effectiveness, although in practice the catalyst, such as $\text{Fe}(\text{SO}_4)_2$, $\text{Cu}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$ or $\text{Ce}(\text{NO}_3)_3$, must be removed or recovered from the treated effluent afterwards to prevent the contamination of the receiving water. The aim of the present work was to gain insights into simultaneous catalytic NB and phenol oxidation, and to provide a working strategy for the degradation of refractory compounds by the batch addition of an initiator. We also expect this strategy to be useful with other active heterogeneous catalysts in the future as a means of accomplishing the economical and environmentally friendly oxidation of pollutants.

2. Experimental

2.1. Materials and reagents

NB and phenol were purchased from Sigma-Aldrich Chemicals. All other chemicals were of analytical grade and were obtained from the Shanghai Chemicals Co. (China), while the solvents were all high performance liquid chromatography (HPLC) grade. Water was prepared with a Milli-Q water purification system (Millipore, Milford, MA) for use in all experimental trials.

2.2. Catalytic wet air oxidation

The reactor was made of stainless steel (SS316) and had an inner volume of 400 mL, and the instrument structure was illustrated in a previous publication [18]. The reaction temperature was measured using a thermocouple and controlled by an intelligent regulator. The autoclave was charged with 200 mL of an aqueous solution in which the initial concentrations of NB

and phenol were 400 and 800 mg/L, respectively. The reactor was subsequently pressurized with pure nitrogen to a pressure of 5.0 MPa and this pressure was maintained for 3 min after which the autoclave was evacuated to 0.1 MPa. This step was repeated three times to make sure that the original oxygen in the reactor was replaced with nitrogen. The reactor was then pressurized to 4.0 MPa with nitrogen and heated to the desired reaction temperature. Once this temperature was reached, pure oxygen (the pressure of which was determined using the equation $pV = nRT$) was supplied to the reactor and the reaction time was counted from this "zero" point. The stir speed was set at 500 rpm to allow for vigorous mixing so as to ensure that the oxidation rate was not controlled by mass transfer effects. Liquid samples were periodically withdrawn and analyzed for phenol and NB levels.

2.3. Analysis

The liquid phase aliquots were analyzed by HPLC (Waters 2690-996 with a photodiode array detector) using a Kromasil C_{18} column (250 mm \times 4.6 mm, 5 μm). The chromatograph was calibrated with standard solutions of NB and phenol in the range of 0 to 500 mg/L and 0 to 1000 mg/L, respectively, producing calibration curves with R^2 values greater than 0.999. The mobile phase was a 60/40 (V/V) water/methanol mixture in the isocratic mode with detection at an absorbance wavelength of 265 nm. The flow rate was set to 1.0 mL/min, and the injection volume was 10 μL . Under these conditions, the retention time of the NB and phenol was 7.3 and 12.9 min, respectively.

3. Results and discussion

3.1. Effect of Cu^{2+} on the catalytic co-oxidation of NB

It has been reported that Cu^{2+} shows good catalytic effects during the WAO of pollutants [13]. Therefore, in this work, we initially assessed Cu^{2+} as a homogeneous catalyst for the co-oxidation of NB and phenol. In a typical trial, a $\text{Cu}(\text{NO}_3)_2$ solution (2 mL, 0.2 mol/L) was added to 200 mL of a solution of NB and phenol, to produce a final Cu^{2+} concentration of 2 mmol/L. Under these conditions, a NB conversion of 91% was achieved after 1 h at 200 °C in the presence of phenol, while only 22% NB conversion was observed without phenol under the same conditions. In contrast, a previous study by our group found minimal NB conversion in the presence of phenol at 200 °C, with only slight improvements to 24% and 27% at 210 and 220 °C [16]. It therefore can be concluded that $\text{Cu}(\text{NO}_3)_2$ is indeed a very active catalyst for the co-oxidation of NB. Given this promising result, we expanded our efforts and screened a number of other homogenous catalysts for the co-oxidation of NB and phenol, examining the effects of the catalyst and the presence of phenol.

3.2. Effect of different homogenous catalysts

The effects of the homogenous catalysts $\text{Fe}(\text{SO}_4)_2$, $\text{Ni}(\text{NO}_3)_2$,

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