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Contaminant degradation by irradiated semiconducting silver chloride particles: Kinetics and modelling



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ABSTRACT

The kinetics and mechanism of light-mediated formic acid (HCOO^-) degradation in the presence of semiconducting silver chloride particles are investigated in this study. Our experimental results show that visible-light irradiation of AgCl(s) results in generation of holes and electrons with the photo-generated holes and its initial oxidation product carbonate radical, oxidizing HCOO^- to form CO_2 . The HCOO^- degradation rate increases with increase in silver concentration due to increase in rate of photo-generation of holes while the increase in chloride concentration decreases the degradation rate of HCOO^- as a result of the scavenging of holes by Cl^- , thereby resulting in decreased holes and carbonate radical concentration. The results obtained indicate that a variety of other solution conditions including dioxygen concentration, bicarbonate concentration and pH influence the availability of holes and hence the HCOO^- degradation rate in a manner consistent with our understanding of key processes. Based on our experimental results, we have developed a kinetic model capable of predicting AgCl(s) -mediated HCOO^- photo-degradation over a wide range of conditions.

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1. Introduction

Organic contaminant elimination from aqueous streams represents a major challenge, particularly for phenolic compounds and azo dyes that are highly toxic and are resistant to biological degradation. Advanced oxidation processes are typically needed for degradation of such recalcitrant contaminants with particular interest shown recently in the use of silver chloride (AgCl(s)) and associated plasmonic silver nanoparticles (AgNPs) given their ability to induce degradation on illumination with visible light [1–7]. Xu and co-workers synthesized Ag@AgCl core-shell assemblages and found that these composite materials degraded methyl orange dye and 4-chlorophenol under visible light irradiation [5]. Other investigators have combined Ag@AgCl assemblages with semiconductors including ZnO [8] and TiO_2 [9] and observed effective degradation of dyes.

Although the effectiveness of Ag@AgCl in inducing contaminant photo-degradation is evident, a definitive mechanism for the degradation process has yet to be confirmed though a variety of possibilities have been suggested [10–13]. There is a particular lack of information on the identity of the oxidizing species inducing degradation, with various studies suggesting involvement of holes

[14], chlorine atom (Cl^0) [5,15], hydroxyl radical (OH^\cdot) [5], superoxide (O_2^-) [5,14], and hydrogen peroxide (H_2O_2) [5] however no definite evidence is provided. Recently, we investigated the mechanism of generation of free chlorine and reactive oxygen species (ROS) on irradiation of unsupported AgCl(s) particles and showed that oxidation of Cl^- by holes results in the formation of Cl^0 which hydrolyses to form free chlorine [16]. Furthermore, ROS including O_2^- and H_2O_2 are formed via reduction of O_2 by photo-generated conduction-band electrons with singlet oxygen ($^1\text{O}_2$), another ROS, generated as a result of the reaction of free chlorine and H_2O_2 [16]. While it is possible that one or more of these reactive species may be involved in the degradation of organics, little attempt has been made to clarify the exact identity of the key oxidant(s).

In the study described here, we investigate the kinetics and mechanism of visible-light driven photo-degradation of formic acid in the presence of AgCl(s) with the aim of determining the roles of ROS, Cl^0 and free chlorine in the degradation mechanism. The reasons for choosing formic acid are three fold. Firstly, it is a simple target organic compound that, on oxidation, forms CO_2 thereby minimizing complications with production of oxidant scavenging intermediates (a problem encountered with the use of chlorinated phenolic compounds). Secondly, unlike dye molecules, it does not absorb visible light and, as such, enables investigation of reactions occurring due to light-absorption by

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AgCl(s) only. Thirdly, formic acid degradation is of interest in its own right since this compound is used in fabric dyeing, printing processes, as a food additive and as a buffering agent in HPLC analysis.

The photocatalyst, Ag@AgCl, used here was generated in-situ with AgNPs formed by photochemical reduction of AgCl(s) which was, in turn, formed by addition of Ag(I) to solutions containing excess NaCl. Various experiments were performed to determine the mechanism of photo-degradation and the identity of the oxidant responsible for photo-degradation. Based on our experimental observations, we have developed a kinetic model that is capable of predicting formic acid degradation rates over a range of solution conditions.

2. Experimental methods

2.1. Reagents

All reagent solutions were prepared using 18 M Ω cm resistivity Milli-Q water unless otherwise stated. All experiments were carried out in 2 mM NaHCO₃ buffer containing NaCl at pH 8 unless specifically stated. All pH values were adjusted with 1 M HNO₃ and 1 M NaOH. A stock solution of 0.5 mM ¹⁴C labelled and 4.5 mM non-labelled sodium formate (HCOONa) was prepared in Milli-Q water. A 50 mM Ag(I) stock solution was prepared by dissolving AgNO₃ in Milli-Q water. An approximately 46 mM NaOCl stock solution was prepared by 20-fold dilution of concentrated sodium hypochlorite (Sigma) and was standardized using the Na₂S₂O₃ titration method [17]. A 4 mM H₂O₂ stock solution was prepared weekly and was standardized by UV spectrometry [18]. A 200 μ M stock solution of citrate stabilized AgNPs was prepared using the method described by He et al [19]. Since free chlorine exists principally as OCl⁻ and formic acid (pK_a ~3.75) exist mostly as HCOO⁻ at pH 8, we use OCl⁻ and HCOO⁻ to represent total free chlorine and formic acid from here on in our discussion.

2.2. Photochemical experimental setup

Photochemistry experiments were performed in a water-jacketed 0.5 L glass reactor covered with aluminum foil to exclude extraneous light. The reaction solution was maintained at 25 \pm 0.5 $^{\circ}$ C with a recirculating water bath. A 300 W Xe arc lamp (Perfectlight Inc, Beijing) equipped with a UV-cutoff filter (λ > 400 nm) was positioned vertically above the reactor to irradiate the sample. The incident photon irradiance of the lamp is shown in Supporting Information (Fig. SI-1). Total sample volume used for analysis was no more than 25 mL (8% of 200 mL); as such, the error introduced by volume change (which alters the light energy flux per unit volume) was minimal.

For HCOO⁻ degradation experiments, AgCl(s) was formed by addition of an appropriate volume of 50 mM Ag(I) stock solution to 200 mL of buffer solution at pH 8.0 containing 2 mM NaHCO₃ and NaCl at particular concentrations. AgCl(s) so formed was continuously stirred and aged for 35 min after which radiolabelled and non-radiolabelled sodium formate were added such that final concentrations of 0.1 μ M H¹⁴COO⁻ and 0.9 μ M H¹²COO⁻ were achieved in solution and irradiation then commenced.

2.3. AgCl(s) characterization

AgCl(s) particles were characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) with these methods enabling elucidation of the shape, size and surface structure of the nano-sized specimens. The samples were prepared as described in our earlier work [20].

2.4. Formic acid measurement

Oxidation of HCOO⁻ leads to the production of CO₂ that, if the pH is low enough, can be readily removed from solution by sparging. As such, quantification of the amount of HCOO⁻ remaining in solution following sparging under acidic conditions provides a measure of the extent of oxidation of this simple target species. For HCOO⁻ measurement, samples were withdrawn from the reactor every 5 or 10 min and immediately mixed with 4 mL of 10 mM HNO₃, 3 mL of which was then centrifuged at 10,000 rpm for 1 min in two 1.5 mL eppendorf tubes. Subsequently, 2 \times 1.0 mL of the supernatant from the eppendorf tubes was removed and placed in scintillation vials, which were then sparged with 99+% argon to drive out any residual CO₂ from the solution. Next, 5 mL scintillation fluid was mixed with 1 mL of sample in the scintillation vial, and the vial placed in the liquid scintillation counter for measurement. A calibration curve was obtained using the procedure described above with known concentrations of H¹⁴COO⁻ and H¹²COO⁻.

2.5. Numerical modeling

Kinetic modelling was undertaken using the kinetics modeling package ACUCHEM [21]. Sensitivity analysis of species concentrations in the model to perturbations to the various rate constants was undertaken using two methods: (i) normalized sensitivity coefficients (NSCs), and (ii) Principal Component Analysis (PCA) on the model as described earlier [20]. The NSCs values were generated using kinetics modeling package KINTECUS [22].

3. Results and discussion

3.1. Characterization of AgCl(s) by SEM and STEM

SEM images of non-irradiated and irradiated AgCl(s) in the absence and presence of formic acid are shown in Fig. 1. As shown, the non-photolyzed AgCl(s) particles are mostly cubic with the particles size in the range 650 nm–1.2 μ m. Following irradiation (in the absence of HCOO⁻), the AgCl(s) particles became more poly-disperse with many smaller quasi-spherical particles (sizes ranging around 100–300 nm) present on the surface of the larger (presumably AgCl(s)) particles. When AgCl(s) was irradiated in the presence of 1 μ M HCOO⁻, particles falling into two size ranges were clearly evident (see Fig. 1c), with one cohort of quasi-spherical particles exhibiting diameters from 100 nm to 300 nm and a second cohort exhibiting diameters ranging from ~500 nm to 650 nm. Some particles of diameters greater than 1 μ m were also present, and were comprised mainly of cubic or semi-cubic particles. These larger cubic particles appear similar to the dark-aged AgCl(s) particles while the newly-formed smaller sized particles (d < 300 nm) possibly correspond to AgNPs formed on reduction of Ag(I) by photo-generated electrons as suggested in other studies [4,5,10,14,23,24]. These AgNPs are formed with much greater abundance in the presence of HCOO⁻ possibly since the presence of HCOO⁻ will reduce the rate of electron-hole pair recombination since the photo-generated hole and/or its initial reaction product will be consumed by reaction with HCOO⁻. Removal of holes in this manner will result in a higher steady state concentration of conduction band electrons and an increase in the rate of reduction of Ag(I) to Ag⁰ with these silver atoms presumably coalescing to form AgNPs.

To establish that the Ag⁰ content of our samples increases on irradiation, we further performed element mapping and Energy Dispersive X-ray spectroscopy (EDX) analysis. Although no quantitative analysis was attempted, as the samples are of similar

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