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Fenton-Like Oxidation of 4−Chlorophenol: Homogeneous or Heterogeneous?

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Abstract

Heterogeneous Fenton-like catalysts have received considerable research attention because they could potentially be attractive for oxidative removal of organic contaminants from tertiary wastewater. However, process design is still hampered by insufficient understanding of the chemical pathways involved, and especially whether oxidation activity stems from heterogeneous surface chemistry or minute concentrations of dissolved metal ions in the homogeneous phase. Using inductively coupled plasma-optical emission spectroscopy (ICP-OES) in combination with pH monitoring and ultraviolet-visible spectroscopy (UV-Vis) we have monitored the degradation of 4-chlorophenol (4-CP) over two Fenton-like heterogeneous systems, namely FeO_x supported on TiO_2 and $CuFe_2O_4$. We show conclusively that these systems proceed predominantly through a homogeneous route via dissolved metal ions from the solid phase catalysts. Control experiments with homogeneous Fe^{3+} or Cu^{2+} systems reveal that even minute concentrations (μM/sub-ppm) of dissolved metal ions leached from the solid phases account for the observed 4-CP degradation rates in the heterogeneous systems. ICP-OES revealed that metal leaching was time-dependent and variable because of pH variations associated with changing acid release rates. Buffering solutions at pH 7.4 suppressed metal leaching (and hence 4-CP degradation) in the FeO_x/TiO_2 system, but not in others. For example, pH buffering did not entirely suppress metal leaching from $CuFe_2O_4$, for which 4-CP degradation was retained through small concentrations of Fe and Cu ions in solution. Our results highlight the importance of careful monitoring of metal content in the aqueous phase, certainly with analytical sensitivity below ppm concentrations of the dissolved metals, and also the crucial influence of time-dependent pH variations on the reaction process. Recyclability of catalysts, pH buffering of solutions or monitoring of metal content in the solid phase by less sensitive analytical methods, e.g., chemical analysis, gravimetry, X-ray fluorescence, or energy dispersive X-ray analysis in electron microscopes, cannot exclude the homogeneous Fenton route in the presence of solid catalysts.

Keywords

Fenton-like, 4-chlorophenol, $CuFe_2O_4$, leaching, homogeneous, heterogeneous, catalysis

1 Introduction

Fenton's reaction is an efficient way for treating organic contaminants, e.g. for soil remediation,[1] oil spill clean-up,[2] and industrial wastewater treatment.[3] Through the addition of Fe^{2+}, H_2O_2 and acid to wastewater streams OH radicals ($^{\bullet}OH$) can be generated through the oxidation of Fe^{2+} (Fenton's reaction, eq. 1). $^{\bullet}OH$ is the active species that degrades organic contaminants.[4] Fe^{2+} can then be regenerated by $HO_2^{\bullet}$, completing the Haber-Weiss reaction (eq. 1 and eq. 2).[3]

$$Fe^{2+} + H_2O_2 \rightleftharpoons Fe^{3+} + {}^{\bullet}OH + OH^- \qquad \text{eq. 1}$$

$$Fe^{3+} + HO_2^{\bullet} \rightleftharpoons Fe^{2+} + O_2 + H^+ \qquad \text{eq. 2}$$

Fenton's reaction proceeds optimally around pH 3, thus wastewater streams need to be acidified.[5] Subsequent neutralisation leads to $Fe(OH)_3$ precipitates as a sludge, requiring an additional separation step.[6] This complexity of the homogeneous Fenton route motivated investigations of heterogeneous Fenton-like systems, seeking to localise the Fenton process at the surface of a solid phase containing the required metal ions. For the remainder of this paper we will use the labels "homogeneous" and "heterogeneous" in this sense, i.e., referring to the physical phase containing the active metal species, rather than homogeneity or heterogeneity in the distribution of active sites on the solid phase or in the liquid phase. The rationale underlying the search for heterogeneous Fenton-like system is that the solid phase may stabilise active metal species, so that the additional step of metal ion precipitation is not necessary and catalysts can be re-used. Also, the operational pH range can be widened as the local pH may be modified by the solid supports.[6, 7] On the downside, mass transport limitations in heterogeneous processes can be considerable. Examples of simple Fenton-like solid catalysts are Fe (oxy)hydroxides e.g., magnetite, ferrihydrite and hematite.[5, 6, 8] Also attractive is magnetite (Fe_3O_4), which can be easily separated from the solution through its magnetism. The impact on catalytic activity of replacing Fe^{2+} ion in the inverse spinel structure of Fe_3O_4 by other ions such as Cu^{2+}, Co^{2+}, Mn^{2+} and Ni^{2+} has also been explored.[9]

Currently, rational process design is still hampered by insufficient mechanistic information about heterogeneous Fenton-like reactions. Studies of heterogeneous Fenton-like reactions have focused on kinetics and catalyst stability rather than deeper process analytical understanding.[6, 7] Crucially, most heterogeneous Fenton-like catalysts leach some metal ions into the aqueous phase,[6] raising the question whether the sites of the Fenton reaction are metal ions in the solid phase or the leached metal ion species dissolved in the homogeneously aqueous phase. This "homogeneous or heterogeneous problem" is by no means unique in catalysis[10, 11] and is often not straightforward to address. Complications in identifying the correct chemical pathway could arise because dissolved homogeneous species can deactivate and re-deposit as a solid phase, especially when pH variations occur as a result of the reaction. In the case of Fe and Cu based Fenton-like catalysts, leaching of metallic species is favoured in acidic and mildly heated aqueous solutions.[12] With a combination of such complicating factors at play, gathering evidence for the presence of a heterogeneous catalytic route requires a very careful approach.

The nature of the active species in heterogeneous Fenton-like systems thus remains largely unresolved. Active species have been reported as either homogeneous,[13-15] heterogeneous,[16-21] or a combination of both,[22-27] while some work assumed that the reactions proceeded through a heterogeneous route.[28-33] Approaches that have been used to ascertain the presence of heterogeneous catalytic routes have included: (i) re-using filtered solutions and checking for organic degradation;[17, 21, 34] (ii) buffering solutions at alkaline/near-neutral pH to prevent metal ions leaching;[19, 20] (iii) comparing organic degradation kinetics in homogeneous and heterogeneous catalytic systems;[35] and (iv) quantification of the amount of leached metal ions. When metal ion concentrations are found to be small or below detection limit, the reactions are often assumed to be heterogeneous.[9, 17, 19, 20]

4-chlorophenol (4-CP) is an often used model contaminant in wastewater treatment research. Chlorophenols are toxic and recalcitrant contaminants that are widely used as intermediates in pesticide, dye and chlorinated phenol synthesis. They are antimicrobials, and applied as fungicides to freshly-cut wood and in a wide range of other products, including oils, adhesives, textiles, leather and pharmaceutical products.[36] Using the Fenton-like degradation of aqueous 4-CP as the model system we have set out to establish a protocol of analytical measurements and control experiments that can conclusively address the possibility of a homogeneous route via metal ions leached from heterogeneous Fenton-like systems. We used iron oxide (FeO_x) catalysts supported on TiO_2 (FeO_x/TiO_2) as well as the substituted spinel phase $CuFe_2O_4$ as test systems, but we believe that the conclusions we will draw for Fe and a Fe/Cu-based heterogeneous catalysts may well be transferable to other Fenton-like systems (including photo-Fenton-like and sono-Fenton-like systems).

2 Experimental

The chemicals were used without further purification: 4–CP (±99%, puriss, Aldrich), H_2O_2 (Aldrich, 35 wt% in water), TiO_2 (Evonik P25), $Cu(NO_3)_2$ (Sigma-Aldrich, >99.99%), $Fe_2(SO_4)_3$ (Sigma Aldrich, 97%), and pH 7.4 phosphate buffer tablets (Sigma). Deionised water from Millipore DirectQ-UV system was used throughout this work.

The FeO_x/TiO_2 catalysts were synthesised using a deposition-precipitation method.[37, 38] TiO_2 powder was first mixed with a $Fe_2(SO_4)_3$ solutions to result in Fe loadings of either 1 wt% or 10 wt%. The stirred slurry was heated to 85°C over a period of 50 min and then kept constant for another 40 min.

The mixture was filtered, washed several times with water and dried overnight in an oven at 70°C. The powder was then calcined in a muffle furnace at 300°C for 5 h with 5 L min^{-1} flow of air.

The $CuFe_2O_4$ catalyst was synthesised using a co-precipitation method.[39] A solution containing $Fe_2(SO_4)_3$ and $Cu(NO_3)_2$ with 2:1 Fe to Cu molar ratio was adjusted to pH 12 by dropwise addition of NaOH to precipitate both metals. The solution was then stirred for 2 h at 90°C. The mixture was filtered, rinsed with water and dried overnight in an oven at 70°C. The catalyst was then calcined in a muffle furnace at 600°C for 4 h. Powder X-ray Diffraction (XRD) patterns of the catalyst showed that the synthesised catalyst was indeed $CuFe_2O_4$ (Figure S1 in the supporting information).[40]

An open glass reactor system (Radley's carousel 6 plus) was used for running the Fenton-degradation tests (Figure S5 in the supporting information). Cooling water was circulated through the reflux head to minimise reactant loss by evaporation. The glassware was cleaned thoroughly using detergent and water, then rinsed with deionised water before use. For 4-CP Fenton degradation the solutions were kept at 60 ± 2°C and stirred using magnetic stirrer bars. Each reactant solution contained 150 mL of 0.48 mM 4-CP and 16 mM H_2O_2. The catalysts were either 1 g L^{-1} of the solid catalyst (FeO_x/TiO_2 or $CuFe_2O_4$) or, in the case of the homogeneous catalysts, 0.9, 5.4 μM $Fe_2(SO_4)_3$ or 15.3 μM $Cu(NO_3)_2$solutions. Reactions were initiated after the addition of H_2O_2 to the reaction solutions. All samples were filtered with 0.1 μm syringe filters before analysis. Visible light is known to affect 4-CP degradation in Fenton and TiO_2 systems.[41-43] To rule out any possibility that ambient light illumination (room lighting/sunlight) causing photocatalysis, all reactions were carried out in the dark, in a fumehood with all openings covered by Al foil.

In control tests with 150 mL of 0.48 mM 4-CP at 60°C, 4-CP degradation was negligible over a period of 8 h (Figure S2). The pH change was negligible (5.87 to 5.78) compared to typical reactions where 4-CP were fully degraded (~5 to 3.3). The negligible 4-CP degradation and the lack of a pH change indicate that (i) 4-CP loss due to evaporation was negligible at 60°C and (ii) the cleaning method was sufficient to remove most trace reactants from previous reactions.

H_2O_2 itself is a strong oxidant for the degradation of organics,[4] and its oxidation activity is known to be enhanced by unwanted introduction of trace metal (Fenton/Fenton-like reactions) contaminants, UV irradiation (including ozone formation), microwaves, ultrasound (sonolysis), or a combination of such processes,. To determine the extent of 4-CP degradation by H_2O_2 alone, controls were run with 0.48 mM 4-CP and 16 mM H_2O_2 without the presence of added metal catalysts. At 60°C, 4-CP was degraded by H_2O_2, but at less than half the rate of the Fenton-like reactions (Figure S3).

Dissolved Fe and Cu concentrations in the homogeneous aqueous phases were determined using a Varian Vista-PRO axial inductively coupled plasma-optical emission spectroscopy (ICP-OES). The detection limits were 1×10^{-4} ppm (1.8×10^{-6} mM) for Fe and 3×10^{-4} ppm (4.7×10^{-6} mM) for Cu.[44] A carefully calibrated Mettler-Toledo S220 SevenCompact pH meter was used for determining H^+ concentrations.

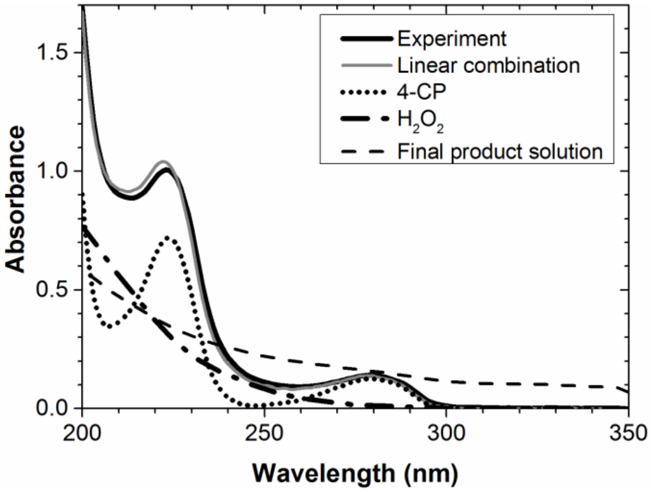


Figure 1. Example of a UV-Vis spectrum modelled by linear combination of the spectra from pure 4-CP, H_2O_2 and the final product solution.

A Beckman Coulter DU520 UV-Vis spectrometer was used to monitor 4-CP degradation. Using reference spectra of solutions containing pure reactants and the final products, the UV-Vis spectra could be analysed to obtain 4-CP concentration profiles (Figure 1). The experimental spectra were thus modelled as a linear combination of spectra from the species present in the solution: 4-CP, H_2O_2 and the final product products (eq. 3).

$$\text{Linear combination spectrum} = x_1[\text{4-CP}] + x_2[H_2O_2] + x_3[\text{final product solution}] \qquad \text{eq. 3}$$

Using the generalised reduced gradient method in Microsoft Excel, scaling factors x_i were optimised and 4-CP concentrations quantified. Error bars were estimated by correlating the sum of the differences between experimental and calculated linear-combination spectra (in absorbance unit) with 4-CP concentrations. The main source of error stems form the adequacy of the reference solutions used in the linear combination fitting. There was evidence that unidentified intermediate species did contribute to the experimental spectra but with tolerably low intensities, as they are comparatively weakly absorbing in the UV range.

3 Results

3.1 FeO_x/TiO_2 Catalysts

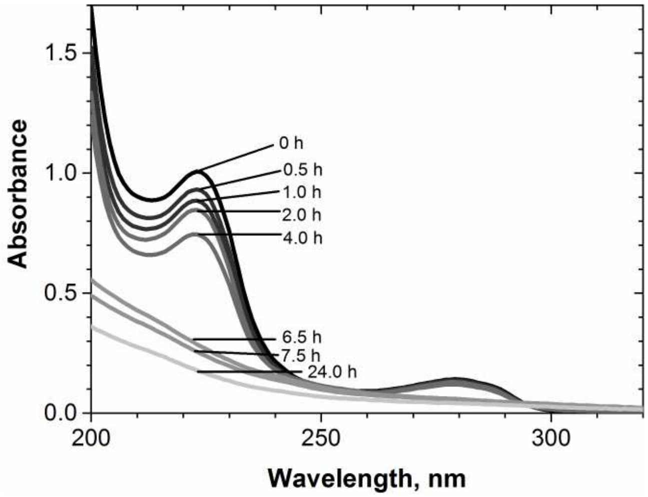


Figure 2. Reaction progress monitored using UV-Vis spectroscopy in the solution containing 16 mM H_2O_2, 0.48 mM 4-CP and 1 g L^{-1} FeO_x/TiO_2 (1 wt% Fe) at 60°C.

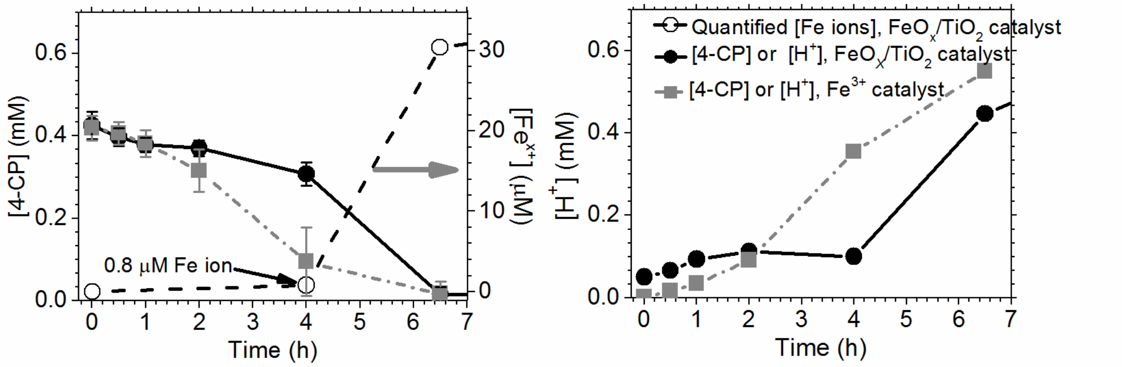
Figure 2 contains a representative sequence of UV-Vis spectra obtained for 4-CP degradation using FeO_x/TiO_2 (1 wt% Fe) catalyst. The decrease in 4-CP concentration is most evident from the intensity in the wavelength ranges at around 225 and 280 nm. The 4-CP concentrations obtained from the linear combination analysis are shown as solid lines in the left column of Figure 3a. After 4 h, ~28% of 4-CP was degraded, while complete degradation was achieved after 6.5 h. The H^+ concentration (shown on the right in Figure 3a, solid line) gradually increased approximately with the stoichiometry expected from the formation of one HCl per decomposed 4-CP molecule. ICP-OES indicated that the Fe ion concentration in the homogeneous phase leached from the FeO_x/TiO_2 (1 wt% Fe) catalyst was 0.8 μM after 4 h and increased to 30 μM after 6.5 h (black dashed line in Figure 3a). This corresponds to an increase of Fe ion concentration from 0.045 ppm (0.7 mol% of the theoretical Fe content on 1 wt% FeO_x/TiO_2) after 4 h to 1.7 ppm (34%) after 6.5 h.

To examine the possibility that the presence of Fe ions at such low concentrations is sufficient to result in 4-CP degradation, a control experiment was carried out using 0.9 μM of dissolved Fe^{3+} as a homogeneous catalyst and without the presence of heterogeneous FeO_x/TiO_2 catalyst. The resulting 4-CP and H^+ profiles using the homogeneous Fe^{3+} catalyst (Figure 3a, grey dashed lines) were very similar to those obtained from the FeO_x/TiO_2 system (Figure 3a, black solid lines) suggesting strongly that 4-CP degradation in the Fenton-like FeO_x/TiO_2 system was mainly due to homogeneous catalysis. In fact, reaction was overall faster in the homogeneous Fe^{3+} system because the initial Fe^{3+} concentration was 0.9 μM while in the FeO_x/TiO_2 system, that concentration was achieved only after 4 h of reaction. These results clearly indicate that a contribution of the homogeneous route in the FeO_x/TiO_2 catalytic system is likely to be significant.

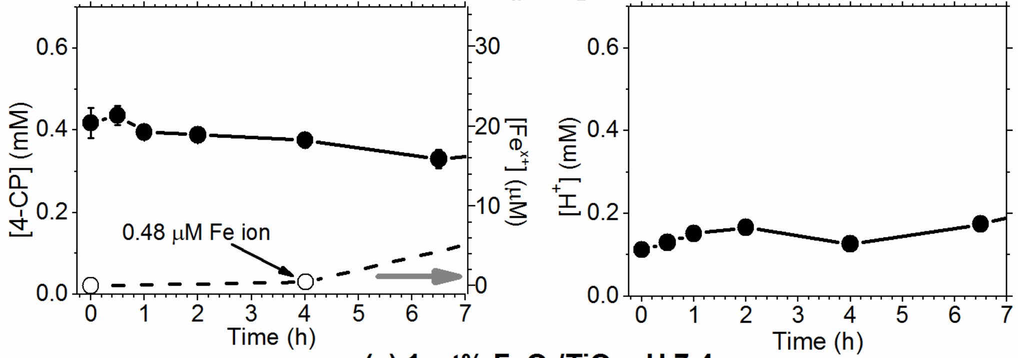
When the 1 wt% FeO_x/TiO_2 catalyst was replaced with the 10 wt% FeO_x/TiO_2 catalyst, only around 20% of the 4-CP was degraded after 6.5 h (Figure 3b), which was much slower compared to the 1 wt% FeO_x/TiO_2 catalyst where most of the 4-CP had been decomposed within the same period of time. It took more than 6.5 h but less than 24 h for the 10 wt% FeO_x/TiO_2 catalyst to degrade most of the 4-CP (Figure S4 in the supporting information). The ICP-OES and pH analysis reveal that the slower 4-CP decomposition stems from a much lower increase in H^+ and Fe ion formation in the homogeneous phase; the Fe ion concentration was 0.48 μM (0.027 ppm, 0.07%) at 4 h and reached 32 μM (1.8 ppm, 2.4%) after one day (Figure S4 in the supporting information). This final metal content in the homogeneous phase was very similar to that of the 1 wt% FeO_x/TiO_2 catalytic system after 6.5 h of reaction (30 μM, 1.7 ppm).

Interestingly, a two-step reaction was observed when using the 1 wt% FeO_x/TiO_2 catalyst, but not for the case of 10 wt% catalyst. The two-step reaction is reminiscent of a previous study using a heterogeneous zero-valent iron system for 4-CP degradation.[27] We observed slow initial changes in 4-CP, H^+ and Fe ion concentrations up to 2 h, but at the later stage, where Fe ion release into the homogeneous phase is increased, 4-CP degradation increased in parallel. This may suggest that the dissolution of Fe ions was auto-catalytic, with the H^+ released by 4-CP degradation accelerated Fe dissolution and further 4-CP degradation. In line with the hypothesis, when we buffered the solution at neutral pH, the changes in 4-CP and H^+ were negligible (Figure 3c), which can be attributed to the suppression of Fe ion dissolution in the near-neutral pH solution. Considering previous work[19, 25, 45] addressing the pH influence we note that manipulating the initial pH instead of buffering the solutions may not be sufficient to prevent leaching because solutions would gradually become more acidic; HCl and organic acids are the reaction intermediates/products of 4-CP degradation.[46]

(a) 1 wt% FeO_x/TiO_2 (heterogeneous) vs. Fe^{3+} catalysts (homogeneous), unbuffered



(b) 10 wt% FeO_x/TiO_2, unbuffered



(c) 1 wt% FeO_x/TiO_2 pH 7.4

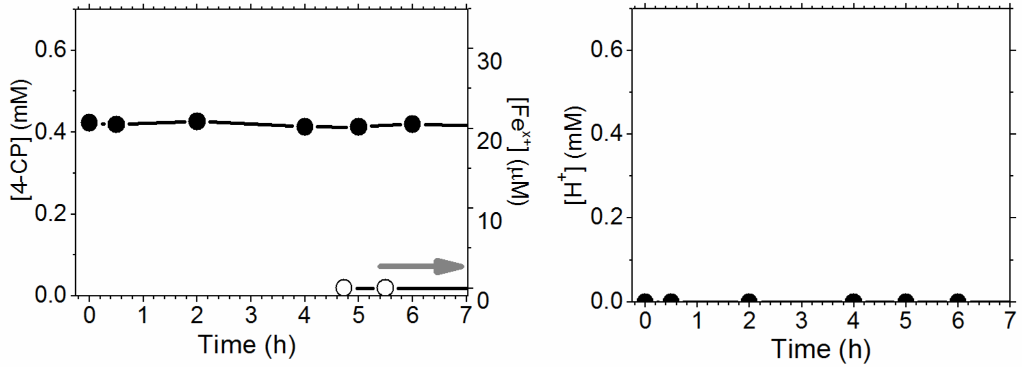


Figure 3. 4-CP degradation using various Fe catalysts. (a) The solid phase catalyst FeO_x/TiO_2 (1 wt% Fe, black lines) and the homogeneous catalyst 0.9 μM $Fe_2(SO_4)_3$ (grey lines). (b) FeO_x/TiO_2 (10 wt% Fe) catalyst. (c) FeO_x/TiO_2 (1 wt% Fe) catalyst in a solution buffered at pH 7.4. Reactions were carried out at 60°C with the reactant solutions containing 16 mM H_2O_2 and 0.48 mM 4-CP.

3.2 $CuFe_2O_4$ Catalysts

$CuFe_2O_4$ catalysts were also tested for 4-CP degradation and the presence of low-level metal leaching was quantified using ICP-OES. Most of the 4-CP was degraded within 0.5 h regardless whether the solutions were buffered or not, or whether the catalysts were calcined or not (Figure 4a, 4c and 4d).

The explanation for the relative pH insensitivity is that Cu dissolution from $CuFe_2O_4$ catalysts is less suppressed than Fe dissolution at near-neutral pH. Indeed, using 15.3 μM (0.97 ppm) Cu^{2+} as a catalyst in a homogeneous control experiment (Figure 4b), 4-CP degradation was similar as in the $CuFe_2O_4$ system, for which ICP-OES indicated that it released a similar concentration of Cu into the homogeneous phase. This suggests that the dissolved homogeneous Cu ions are sufficient to explain the observed catalytic decomposition of 4-CP in the $CuFe_2O_4$ system.

Catalyst calcination and pH buffering did somewhat suppress leaching of Cu ions, but the Cu concentration in homogeneous phase was still high enough to facilitate 4-CP degradation. For the three experiments using $CuFe_2O_4$ catalysts that were buffered at pH 7.4, the concentrations of dissolved metal ions increased initially but eventually decreased after 4-CP was completely degraded. (Figure 4c and 4d). Note that the initial 4-CP concentrations at time = 0 h in Figure 4 were less than the initial 0.48 mM and varied from experiments to experiments. It was especially low in the experiment using 15.3 μM (0.97 ppm) Cu^{2+} catalyst (Figure 4b); likely caused by rapid 4-CP degradation in the presence of homogeneous Cu^{2+} ion. The reaction must have had progressed significantly within the time period from H_2O_2 addition (time = 0 h), sampling, filtration to dilution for UV-Vis measurement which typically takes less than 10 min.

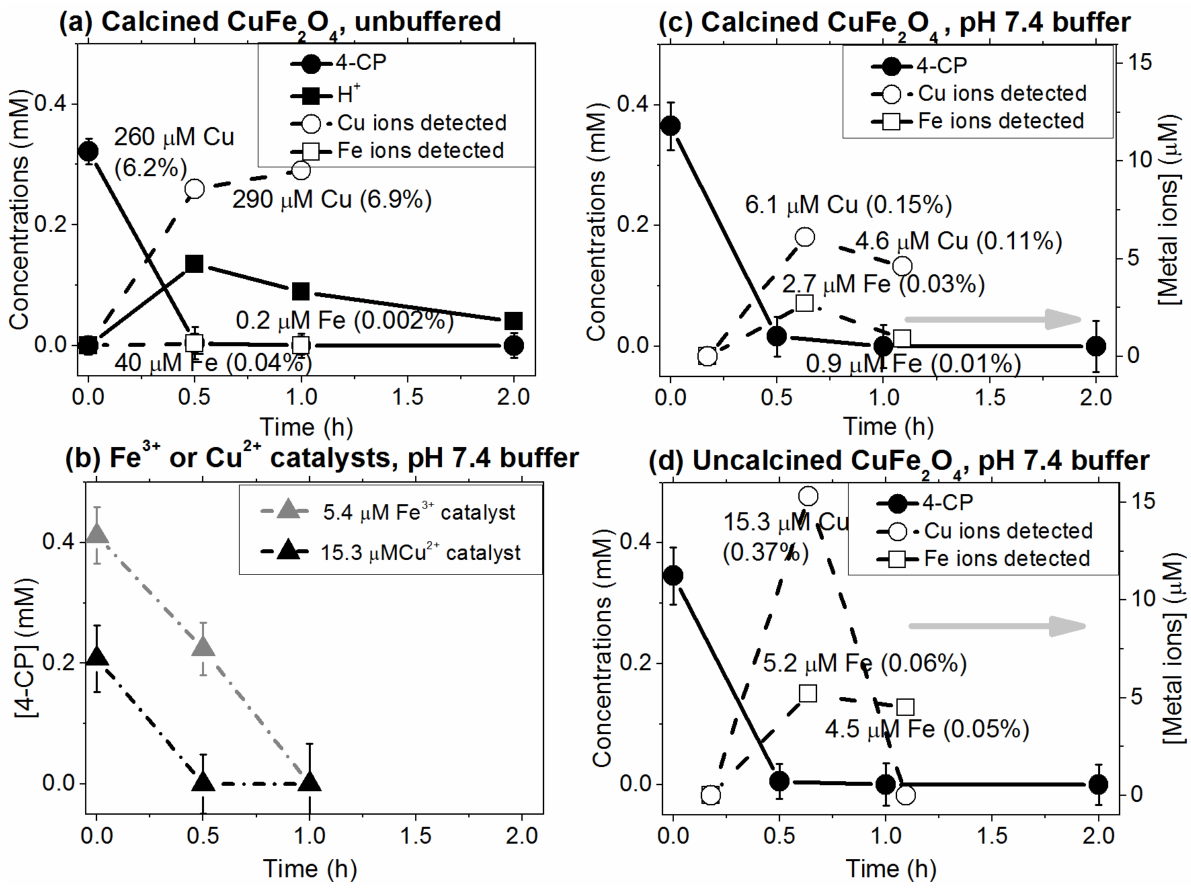


Figure 4. 4-CP degradation using (a) 1 g L^{-1} calcined $CuFe_2O_4$ catalyst in an unbuffered solution, (b) 5.4 μM $Fe_2(SO_4)_3$ or 15.3 μM $Cu(NO_3)_2$ catalyst in a pH buffered solution (c) 1 g L^{-1} calcined $CuFe_2O_4$ catalyst in a pH 7.4 buffered solution, and (d) 1 g L^{-1} uncalcined $CuFe_2O_4$ catalyst in a pH 7.4 buffered solution. The percentages given in parentheses refer to the percentages of leached metal ions compared to the theoretical metal contents on the catalysts. Reactions were carried out at 60°C with the reactant solutions containing 16 mM H_2O_2 and 0.48 mM 4-CP. The $CuFe_2O_4$ catalysts were either uncalcined or calcined at 600°C.

4 Discussion

Tests for the presence of heterogeneous Fenton-like reactions

In previous studies of Fenton-like systems for the degradation of organic compounds it was concluded that the systems are heterogeneous when low or no metal ion concentrations were detected.[9, 17, 19, 20] For the systems that we have examined, our results clearly demonstrate that it is important to use sensitive analytical techniques for quantifying trace metal concentration in the aqueous phase, because even sub-ppm levels of Fe and Cu ions can be responsible for observed 4-CP degradation rates. Moreover, at acidic conditions, Fe dissolution is favoured over the insoluble Fe oxide/hydroxide phases.[47] Another common test used in the literature for studying the role of dissolved metal ions is to filter off the catalysts after reactions, then refill the filtered solutions with reactants and H_2O_2. Reactions were concluded to be heterogeneous when the organics were not degraded.[21] However, uncertainty arises because dissolved Fe ions could be deactivated by forming complexes with organic intermediates.[46] Thus, negligible organic degradation reaction in such tests might well be due to deactivated homogeneous Fe ions species and not necessarily evidence for the presence of a heterogeneous catalytic route.

Fe ions speciation

Although ICP-OES can be used to quantify the concentration of dissolved metal, it cannot determine their oxidation state and is thus not tailored for speciation studies. Other methods are required to determine whether the dissolved Fe species are active or inactive for Fenton's reaction. At the reaction conditions used in our work (aqueous solution containing Cl^-), it is possible that the Fe ions exist as a mixture of free Fe ions, Fe chlorides and Fe hydroxides with Fe hydroxides formation favoured at higher temperature;[41] free Fe ions could possibly be the only species active for homogeneous Fenton reaction with 4-CP. In the experiments using dissolved Fe ion as the catalyst (Figure 3a), 4-CP can be fully degraded, showing that the amount of free Fe ions available is sufficient to induce the Fenton reaction seen with the heterogeneous systems. Fe ion speciation in the homogeneous system may be similar to the dissolved species in the heterogeneous systems, because of the similar reaction conditions in both cases (temperature, 4-CP concentration, i.e. the source of Cl^- and H^+), but it is difficult to come to firm conclusions in the absence of positive speciation evidence. We note that the application of incisive chemical speciation probes such as X-ray absorption spectroscopy[48] currently requires significantly higher concentrations of metal species than encountered in the studies reported here. Studies with mass spectrometric techniques, e.g., electrospray ionization mass spectrometry (ESI-MS), may be able to identify the nature of the solutions species, but were not available for this study.

Buffered solutions tests

Neutral/near-neutral pH slows down leaching of Fe from its oxides and hydroxides. For this reason, pH buffering has often been used to ascertain the presence of a heterogeneous catalytic route in solid Fe-based systems.[17, 20, 23] For the FeO_x/TiO_2 catalysts investigated here, 4-CP was not degraded at all (Figure 3c) when the solution was buffered at pH 7.4, showing that in our case any heterogeneous route at this pH was negligible. On the other hand, 4-CP was fully degraded by small Fe^{3+} concentrations in a homogeneous phase control experiment at buffered pH 7.4 (Figure 4b), suggesting that iron hydroxides formation[49, 50] was insufficient to completely inhibit Fenton's reaction. We note, however, that by merely varying the solution pH not only metal ion leaching is modified; other transformations in the Fenton system are affected too. Above neutral pH, the reaction of $^{\bullet}OH$ with OH^- or H_2O_2 could dominate, thereby decreasing the availability of $^{\bullet}OH$.[19] Electrostatic charge at catalysts surface could vary with pH,[51] affecting sorption of chemicals on the catalyst surface and thus degradation of the organics.

Degradation mechanism using FeO_x/TiO_2 catalysts

We have shown that for both FeO_x/TiO_2 and $CuFe_2O_4$ catalysts, leached metal ions were sufficient to fully degrade 4-CP and that there was no evidence for a heterogeneous reaction. Metal dissolution could be initiated by H^+ from the formation of HCl and organic acids.[52] For FeO_x/TiO_2 catalysts, metal dissolution could follow eq. 4. Dissolved Fe^{3+} ions then undergo Fenton's reaction (eq. 1 and eq. 2), catalysing 4-CP degradation. Metal dissolution was inhibited when the solution was buffered at pH 7.4 (Figure 3c), in line with the Pourbaix diagram for Fe.[12]

$$FeO_x\ (s) + 2xH^+\ (aq) \rightleftharpoons Fe^{3+}\ (aq) + xH_2O\ (aq) \qquad \text{eq. 4}$$

Degradation mechanism using $CuFe_2O_4$ catalysts

In marked contrast with FeO_x/TiO_2 catalysts, for the $CuFe_2O_4$ catalysts, metal leaching was not suppressed even when the solutions were buffered at pH 7.4. To explain the difference, it is necessary to consider that the reaction solution exists as a Cu–Fe–O–H–Cl equilibrium.[47] $CuFe_2O_4$ could be unstable at near-neutral/acidic solutions; favouring the formation of $CuFeO_2$ (delafossite) and Fe_2O_3. Fe^{3+} and Cu^{2+} ions can be produced as part of the $CuFe_2O_4/CuFeO_2/Fe_2O_3$ equilibria in an aqueous solution (eq. 5 and eq. 6).

$$CuFe_2O_4\ (s) \rightleftharpoons Fe^{3+}\ (aq) + CuFeO_2\ (s) + 4H_2O\ (aq) + 3e^-\ (aq) \qquad \text{eq. 5}$$

$$CuFe_2O_4\ (s) + 2H^+ \rightleftharpoons Cu^{2+}\ (aq) + Fe_2O_3\ (s) + H_2O\ (aq) \qquad \text{eq. 6}$$

$CuFeO_2$ and Fe_2O_3 would subsequently dissolve, forming Cu and Fe ions (eq. 7-9).

$$CuFeO_2\ (s) + 4H^+\ (aq) \rightleftharpoons Cu^+\ (aq) + Fe^{3+}\ (aq) + 2H_2O\ (aq) \qquad \text{eq. 7}$$

$$Fe_2O_3\ (s) \rightleftharpoons 2Fe^{2+}\ (aq) + 4e^-\ (aq) + 1.5O_2\ (aq) \qquad \text{eq. 8}$$

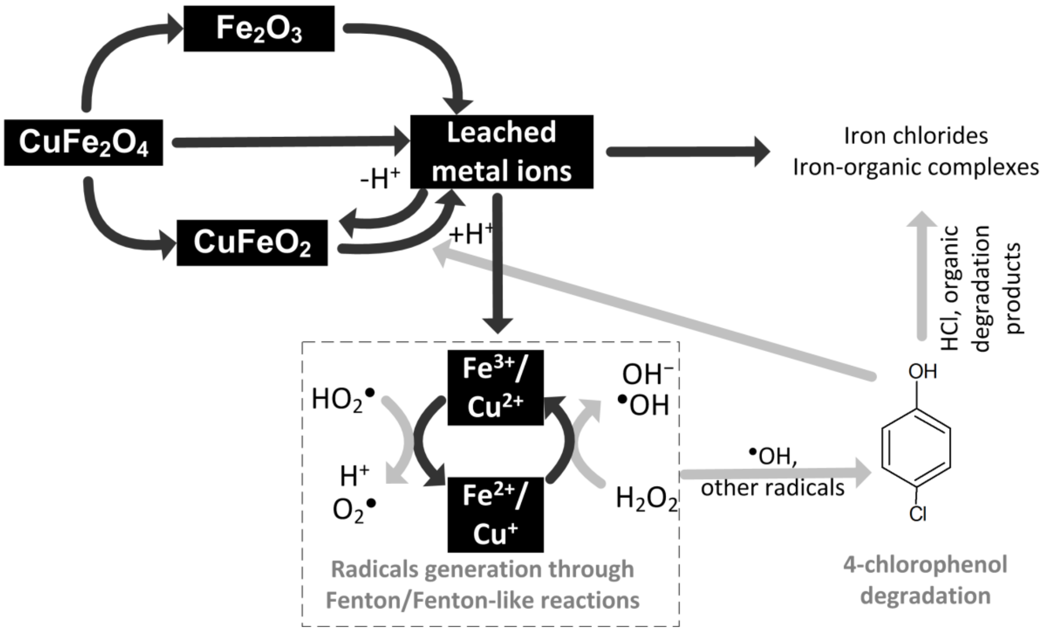
$$Fe_2O_3\ (s) + 6H^+\ (aq) \rightleftharpoons 2Fe^{3+}\ (aq) + 3H_2O\ (aq) \qquad \text{eq. 9}$$

Fe^{2+}/Fe^{3+} would undergo Fenton's and Haber-Weiss reactions as per eq. 1 and eq. 2. Cu^+/Cu^{2+} could undergo equivalent reactions (eq. 10 and eq. 11). Both Fe and Cu ions would then generate $^\bullet OH$ from H_2O_2 which would in turn oxidise organic contaminants in a $CuFe_2O_4$ system.

$$Cu^+\ (aq) + H_2O_2\ (aq) \rightleftharpoons Cu^{2+}\ (aq) + {}^\bullet OH\ (aq) + OH^-\ (aq) \qquad \text{eq. 10}$$

$$Cu^{2+}\ (aq) + HO_2^\bullet\ (aq) \rightleftharpoons Cu^+\ (aq) + O_2\ (g) + H^+\ (aq) \qquad \text{eq. 11}$$

It is interesting to note that Fe and Cu ions concentrations decreased after 4-CP was fully degraded in the buffered solutions but not when the pH was allowed to vary freely (Figure 4). The decrease in metal ion concentrations could be due to metal re-deposition when the supply of H^+ (from 4-CP degradation) depleted, possibly undergoing the reverse reaction of $CuFeO_2$ dissolution (eq. 7). The presence of Cl^- would further favour metal ions dissolution through the formation of Fe and Cu chlorides, which may or may not be active for $^\bullet OH$ generation. The overall relation between metal dissolution and 4-CP degradation is illustrated in Scheme 1. Although not determined here, 4-CP organic degradation products in Fenton/Fenton-like systems are known to be 4-chlorocatechol, catechol, hydroquinone and maleic acid.[27, 45]



Scheme 1. Dissolution of $CuFe_2O_4$ catalysts and the relation between dissolved metal ions and 4-CP degradation. 4-CP degradation products were not determined in this study.

Conclusions

Combined analysis of 4-CP decomposition rates, pH and leached metal content in the homogeneous phase over the Fenton-like heterogeneous catalysts FeO_x/TiO_2 and $CuFe_2O_4$ indicates sub-ppm levels of Fe and Cu ions dissolved from the solid phases are sufficient to explain the observed 4-CP degradation rates. 4-CP reaction rates were affected by time-dependent metal leaching, which is caused by pH variations associated with acidic 4-CP decomposition products. Buffering solutions at pH 7.4 suppressed metal leaching from 1 wt% FeO_x/TiO_2 and thereby 4-CP degradation. Dissolution of Cu from $CuFe_2O_4$ is much less affected at the same pH and 4-CP degradation catalysed by dissolved Cu (and some Fe) remained significant. The Fenton-like FeO_x/TiO_2 and $CuFe_2O_4$ systems thus appear to be homogeneous rather than heterogeneous. We conclude that the development of heterogeneous Fenton-like water treatment processes requires careful monitoring of aqueous metal content with analytical sensitivity below ppm concentrations and control experiments. We believe that the conclusions arrived at in this paper may well be applicable for other Fenton-like systems, and are not necessarily limited to Cu and Fe systems. What our work certainly highlights is the fact that monitoring metal content in the solid phase by gravimetry, X-ray fluorescence, electron microscopy and other conventional analytical means is unlikely to be sensitive enough to detect the low metal losses due to leaching.

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Associated Content

Supporting information contains the powder XRD pattern of the synthesised $CuFe_2O_4$ catalyst, 4-CP degradation profiles for the blank test using 16 mM H_2O_2, the reaction profiles as shown in Figure 3 but with longer time scales and a detailed schematic of the glass reactor system. This material is available free of charge via the Internet at http://pubs.acs.org.

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