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Abatement of oxalates catalyzed by Fe-silica structured surfaces *via* cyclic carboxylate intermediates in photo-Fenton reactions

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Novel silica/Fe structured fabrics were observed to degrade oxalates only under light irradiation showing the formation and disappearance of Fe-carboxylates and the concomitant recycling of the resulting Fe-ions back to the structured catalyst surface.

The depletion of oxalic acids in the atmosphere[1] and during the terminal degradation steps of organic compounds[2] involve concentrations of Fe(III)-oxalate complexes sufficiently large to make their photolysis a dominant source of oxidative radicals driving the mineralization in Fenton like processes. Inorganic structured materials like Nafion,[3] Nafion/silica[4] have recently been loaded with Fe-ions to carry out immobilized Fenton photo-assisted degradation of different pollutants. It is our intention to address the molecular mechanism of the photocatalysis with special attention to a) the accelerating effect of the structured silica/Fe to establish the photoreduction kinetics of Fe(III) complex $[\mathrm{Fe(III)(Ox)}_{n\,=\,1-3}]^{\delta-}$ formed during the abatement of oxalate under light irradiation,[5] b) to detect the Fe-carboxylate formed during photodegradation by infrared spectroscopy and, c) to suggest a reaction mechanism consistent with the experimental results obtained when Fe oxalate complex undergoes degradation to CO_2.

Alumino-borosilicate fibres from Vetrotex® (France) containing SiO_2, B_2O_3, MgO, Al_2O_3, K_2O, Na_2O, Fe_2O_3 were treated with HCl at 90 °C to leach out all the non-silica components.[6] The porosity of the starting SiO_2 fabric was considerably increased since the initial porosity of the untreated SiO_2 fabric was too low for any practical use. The samples were rinsed with distilled water and dried in air at 50 °C. The Fe/SiO_2 fabrics were prepared by ion-exchange/impregnation from aqueous solution of $FeCl_3{\cdot}6H_2O$. The fabrics were dried and then calcined at 450 °C for one hour. The photo-catalytic activity of the structured Fe-silica catalysts was evaluated in cylindrical Pyrex flasks (cut-off $\lambda \approx 290$ nm) each containing 70 ml of reagent solution. Fe/SiO_2 fabric strips of 48 cm^2 were placed immediately behind the wall of the reaction vessel. Irradiation of the solutions in the vessels was carried out inside the cavity of a Hanau Suntest. The total organic carbon (TOC) was monitored *via* a Shimadzu 500 instrument equipped with an ASI automatic sample injector.

Infrared attenuated total reflection (IRATR) Fourier transform spectroscopy was applied to the study of Fe-silica structured surfaces. The reflection spectra were recorded on a Bruker IFS 55 FTIR spectrophotometer equipped with a calcium telluride detector and an internal reflection attachment from Harrick Co. X-ray Photoelectron Spectroscopy (XPS) was obtained with a multi-detection electron energy analyser (CL 150). The characteristic peaks of Fe 2p, O 1s, and C 1s were recorded and the background subtraction was performed according to Shirley.[7] During light irradiation the water samples were submitted to ion chromatography-mass spectrometry (IC-MS) analysis[8] and no organic by-products were found that could be assigned to the decomposition of the oxalate precursor.

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Fig. 1a shows the mineralization of oxalate at different pH values under Suntest light. The results obtained show that the mineralization proceeds in acid solution but attains only 50% of the maximum value when a fraction of the Fe^{3+}-ions has precipitated at pH ≥ 4.1. Fig. 1b shows the profile for the Fe^{2+}-ion available in solution during a run at pH 2.75. Other experimental conditions for Fig. 1b were the same as in Fig. 1a. The Fe(III) photoreduction on the EGF/Fe(III) fabrics under light irradiation is seen to increase with irradiation time. After reaching a maximum at ~20 min, a decrease of Fe(II) was observed due to the reaction $\mathrm{Fe(II)} + \mathrm{HO}^{\bullet} \rightarrow \mathrm{Fe(III)} + \mathrm{HO}^{-}$.[9] Fig. 1b shows that after 60 minutes photocatalysis no more than 0.5 mg Fe^{2+} remained in solution along with 1.0 mg Fe^{3+}. The concentration of Fe^{2+}-ions in solution was determined with *o*-phenanthroline and of Fe^{3+} with thiocyanate.

Fig. 2A shows the ATR spectra of EGF/Fe(0.4%) fabric after adsorption of different concentrations of oxalic acid. The

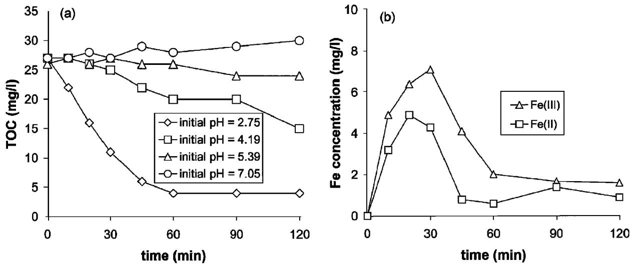


Fig. 1 (a) Mineralization of oxalic acid (1.1 mM) under Suntest light irradiation (86 mW cm^{-2}) in a solution with H_2O_2 (10 mM) as a function of pH in the presence of an EGF/Fe(0.4%) fabric. (b) Concentration of Fe(II) and Fe(III) from a EGF/Fe(0.4%) fabric as a function of time during Suntest irradiation of a solution with the same make up as in Fig. 1a at a pH value of 2.75.

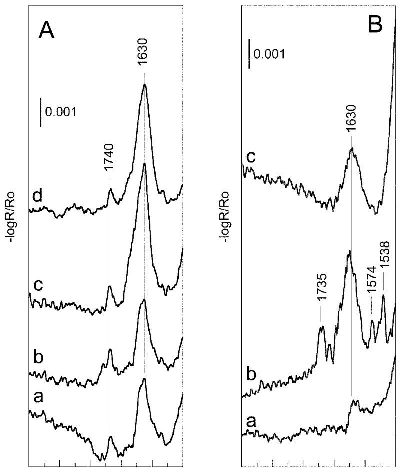


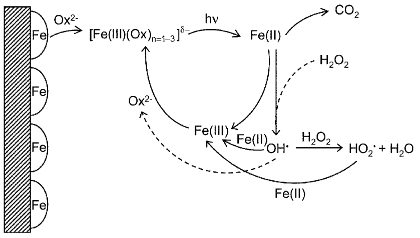
Fig. 2 A) IRATR spectra of EGF/Fe(0.4%) silica fabric equilibrated with different concentrations of oxalates at pH 2.75: a) 0.1 mM b) 1 mM c) 2 mM d) 5 mM. B) IRATR spectra of EGF/Fe (0.4%) silica fabric during Suntest irradiation of a solution of oxalate (1.1 mM) containing H_2O_2 (10 mM) at pH 2.75 after: (a) zero time (b) 15 minutes and (c) 60 min.

strongest band at 1630 cm^{-1} is due to the bending vibration of the OH group of adsorbed water while a low intensity band (with a signal to noise ratio from 5 to 6) at 1740 cm^{-1} reveals the existence of Fe-oxalate surface complexes after oxalate adsorption. The band at 1740 cm^{-1} is assigned to $Fe^{3+}(Ox)_3$ surface complex characteristic of bidentate coordinated and non-coordinated $-COO^-$ carboxy groups on each of the oxalate groups adsorbed on the fabric. This interpretation is based on the similarity with the reported structure of the precipitated Fe^{3+} oxalate hexahydrate.[10] An additional higher frequency shoulder is observed at around 1650 cm^{-1} supporting the formation of the $Fe^{3+}(Ox)_3$ surface complex. The strong band at 1630 cm^{-1} due to the bending vibration of OH group does not allow to estimate the amount of the Fe^{2+} oxalate.

The position of the absorbance bands determined in the samples after adsorption are very different from those reported for the bulk samples: for Fe^{3+} oxalate hexahydrate (1732, 1666, 1614, 1384, 1348, 1264 cm^{-1}) and Fe^{2+}dihydrate (1602, 1383, 1360, 1316 cm^{-1}).[10] The produced surface complex is different from bulk complex due to two reasons: (a) the surface structure is different from the well defined bulk structure since the complex presents linear or two dimensional configuration, (b) the average iron oxidation state is between 2+ and 3+, unlike in the bulk precipitate where well defined Fe^{2+}or Fe^{3+} are possible.

Fig. 2B shows the IRATR spectra of EGF/Fe(0.4%) fabric after different reaction times and reveals the formation of Fe-oxalate surface complexes and their disappearance during the EGF/Fe(0.4%) mediated photodegradation of oxalates. Fig. 2B shows in trace a) the fabric before reaction calcined at 450 °C. The sample after 15 min of reaction shows clearly four absorbance bands at 1735, 1630, 1574 and 1538 cm^{-1}. The strongest band at 1630 cm^{-1} is due to bending vibration of OH groups caused by carrying out the reaction in aqueous solution (adsorbed water). The bands at frequencies 1574 and 1538 cm^{-1} are assigned to the asymmetric stretching vibration of the produced $Fe^{3+}(Ox)_3$ surface complex with bidentate (band at 1574 cm^{-1}) and unidentate (1538 cm^{-1}) surface conformations and with non-coordinated $-COO^-$ carboxy group (1735 cm^{-1}) of oxalate. At 15 min, the maximum the Fe-carboxylate surface complex is observed in Fig. 2B. At 60 minutes, the bands originating either from carboxylic non-coordinated groups or Fe-carboxylate complexes have disappeared. These observations are consistent with oxalic acid and Fe-carboxylate adsorbed on the EGF/Fe(0.4%) fabric being abated during the photocatalysis reported in Fig. 1. The Fe-carboxylate band position and shape at 15 minutes could also indicate the presence of a Fe^{3+}/Fe^{2+} mixed complex with oxalic acid. The disappearance of the characteristic iron surface complexes after 60 min suggests the formation of polymer iron-oxalic surface complex having a lower Fe^{3+}/Fe^{2+} ratio at times shorter than 30 min. This would be in agreement with the results presented in Fig. 1b. Iron is extracted from the EGF/Fe(0.4%) fabric through the formation of $Fe(Ox)_3{}^{3-}$ in dark reactions and through the longer lived metastable intermediate LMCT state$[(C_2O_4)_2Fe\,O_2(CO)_2]^{3-}$ as recently suggested.[1]

Scheme 1 is suggested as the photodegradation pathway for oxalates consistent with the results presented in Fig. 1–2. The LMCT photo-decarboxylation of the Fe-oxalate complex is a fairly common process[9] resulting in the reduction of Fe(III) and evolution of CO_2. As the abatement of oxalate progresses the TOC decreases due to the depletion of the Fe-oxalate and consumption of the oxalic acid in solution. The concentration of Fe(II) also decreases with time as shown by decrease in Fe(II) concentration in Fig. 1b. The hydroxyl and superoxide radicals noted in Scheme 1 become available to the solution due to the added H_2O_2 in the presence of Fe(III)/Fe(II) ions under light irradiation and interact in a series of consecutive reactions leading to oxalate mineralization.



Scheme 1

By estimating the encounter-pair time for the four main reactions following the $[Fe(III)(Ox)_{n\,=\,1-3}]^{\delta-}$ decomposition under light in the presence of H_2O_2 (10 mM), the $OH^\cdot$ formation or consumption probability can be estimated in Scheme 1 from the reciprocal encounter-pair lifetime of the reactions: a) $OH^\cdot + (Ox^{2-}) \rightarrow OH^- + Ox^{-\cdot}$, with $k = 2 \times 10^6\ M^{-1}s^{-1}$ [5] and $[Ox^{2-}] = 10^{-3}$ M, gives a value for the reciprocal encounter-pair lifetime of $\sim 2 \times 10^3\ s^{-1}$ b) $OH^\cdot + Fe^{2+} \rightarrow OH^- + Fe^{3+}$, with $k = 3 \times 10^8\ M^{-1}s^{-1}$ and $[Fe^{2+}] = 7 \times 10^{-5}$ M, the latter value is $\sim 2.1\ 10^4\ s^{-1}$, c) $OH^\cdot + H_2O_2 \rightarrow HO_2{}^\cdot + H_2O$, with $k = 1.3 \times 10^7\ M^{-1}s^{-1}$ [5] and $[H_2O_2] = 10^{-2}$ M, the latter value is $\sim 1.3 \times 10^5\ s^{-1}$ and finally d) $H_2O_2 + Fe^{2+} \rightarrow OH^\cdot + OH^- + Fe^{3+}$, with $k = 47\ M^{-1}s^{-1}$ [2] and $[H_2O_2] = 10^{-2}$ M, the latter value is $\sim 0.47\ s^{-1}$. From reactions a)–c) above, the radical $OH^\cdot$ is mainly consumed by H_2O_2 and not formed by the reaction c) in Scheme 1 since $1.3 \times 10^5\ s^{-1} \gg 0.47\ s^{-1}$. Also it can be estimated that the $OH^\cdot$ radical is consumed by reaction c) and not by reaction a) since $1.3 \times 10^5\ s^{-1} > 2.3 \times 10^3\ s^{-1}$ indicating that only 1% of the $OH^\cdot$ radical reacts with oxalic acid in the presence of H_2O_2 (10 mM). The main decomposition channel of oxalate involves a Fe-carboxylate redox process (see Fig. 2): $[RCO_2\text{-}Fe]^{2+} \rightarrow [R^\cdot] + CO_2 + Fe^{2+}$. Analysis of the amount of Fe extracted of the surface due to oxalate varies between 0.1% and 0.2% of the total Fe available. XPS results confirmed that the depletion of Fe on the fabric increased with the time and concentration of the oxalic acid used. With a 1.1 mM oxalic acid concentration and 18 h equilibration time the Fe^{3+} extracted was 0.2% of the total. The latter value was confirmed by measurements in aqueous solution. The iron remaining on the EFG/Fe(0.4%) fabric surface acts as crystallization nuclei for the Fe-ions returning from the solution due to the overbearing presence of the Fe-loaded fabric in the system under study.[3–5] From the different shapes of the TOC reduction reported in Fig. 1 for runs adding Fe^{2+} (1 mg l^{-1}) or iron in homogeneous solution or added heterogeneously through EGF/Fe(0.4%) fabric, it is possible to suggest that different types of Fe-carboxylates are formed in each case.

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Notes and references

1 Y. Zuo and J. Hoigné, *Environ.Sci.Technol.*, 1992, **26**, 1014.
2 M. Halmann, *Photodegradation of Water Pollutants*, CRC Press, Boca Raton, Florida. 1996.
3 J. Fernandez, J. Bandara, A. Lopez, Ph. Buffat and J. Kiwi, *Langmuir*, 1999, **15**, 182.
4 M. Dhananjeyan, J. Kiwi, P. Albers and O. Enea, *Helv. Chim. Acta*, 2001, **84**, 3433.
5 V. Nadtochenko and J. Kiwi, *J. Chem. Soc., Faraday Trans.*, 1997, **93**, 2373.
6 L. Kiwi-Minsker, J. Yuranov, E. Slavinskaia, V. Zaikovskii and A. Renken, *Catal. Today*, 2000, **59**, 61.
7 A. Shirley, *Phys. Rev.*, 1979, **B5**, 5709.
8 F. Herrera, A. Lopez, G. Mascolo, P. Albers and J. Kiwi, *Appl. Catal. B*, 2001, **29**, 147.
9 Y. Sun and J. Pignatello, *Environ. Sci. Technol.*, 1993, **27**, 304.
10 H. G. M. Edwards and N. C. Russell, *J. Mol. Struct.*, 1998, **443**, 223.