The Ferroin Test: a Sensitive and Convenient Probe of Internal *Versus* External Silver in Microporous Materials: Application to Silver Sodalites

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Ferroin can be used as a sensitive redox active indicator to distinguish conveniently between internally confined and externally located silver aggregates, in a range of silver sodalites, of current interest in advanced materials science applications.

The question of internally confined species *vs.* particles present on the external surface of microporous materials is important in many actual and potential applications, as diverse as catalysis, quantum size effect materials and optical data storage.[1] We have recently studied sodalite based class A, B, C semiconductor component quantum dots and supralattices,[2–4] as well as silver oxalatosodalites as erasable all-optical data storage media.[5,6] For these materials, it has been important to determine whether Ag_4^{p+}, Ag_4X^{q+} and Ag_3^{r+} clusters remain confined in the sodalite lattice, possibly forming an extended array of clusters (denoted a supralattice), or whether silver migrates to the sodalite surface and agglomerates in the form of larger particles. A number of chemical and spectroscopic diagnostic tests for this kind of inside–outside question (methyl viologen$^{2+/1+}$–H_2, $Fe(CN)_6^{3-/4-}$–H_2, XRD, XPS, STEM EDAX, TEM, O_2 adsorption, EPR and NMR relaxation probes) have recently been reviewed by Ozin and Gil.[7] Further possible techniques for the detection of surface silver include surface enhanced Raman spectroscopy (SERS)[8] of either the sodalite framework or specifically adsorbed species, or the observation of an optical plasmon (although the possible existence of an intrinsic tunnelling plasmon absorption[9] associated with internally confined silver moieties of a quantum dot–quantum supralattice could render these latter two tests equivocal). Chemical tests specific for silver or silver ions involve $Cr_2O_7^{2-}$ (to remove external silver), $S_2O_8^{2-}$ (to remove external silver halide) or redox active indicators to actually detect the presence of external silver.

In this communication we report that it is possible to address the question of internal *vs.* external silver using a sensitive chemical size exclusion test involving ferroin as a redox indicator. Ferroin undergoes a colour change from pale blue to red when it is reduced by metallic silver. Since ferroin is too large to enter a sodalite cage (kinetic diameter ~11.6 Å), it can only react with silver on the outside surface of the sodalite (see later). The following redox reactions involved are shown in Scheme 1.

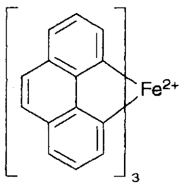
The ferroin complex was prepared by the following method:[10] 1.473 g 1,10-phenanthroline monohydrate (AnalaR) was dissolved in deionized water in a 100 ml volumetric flask. 0.997 g $Fe_2(SO_4)_3{\cdot}nH_2O$ was slowly added, and the solution was made up to the 100 ml mark. Since a brown precipitate formed on standing, aliquots of the supernatant were taken after a very short time, to avoid variations in the ferroin concentration. A fresh solution was used for each set of experiments. 100 µl portions of the supernatant

$$Ag \longleftrightarrow Ag^+ + e^- \qquad E = -0.7996\ V$$

$$(phen)_3Fe^{3+} + e^- \longleftrightarrow (phen)_3Fe^{2+} \qquad E = +1.06\ V$$

pale blue red

$(phen)_3Fe^{2+}$ =



Scheme 1

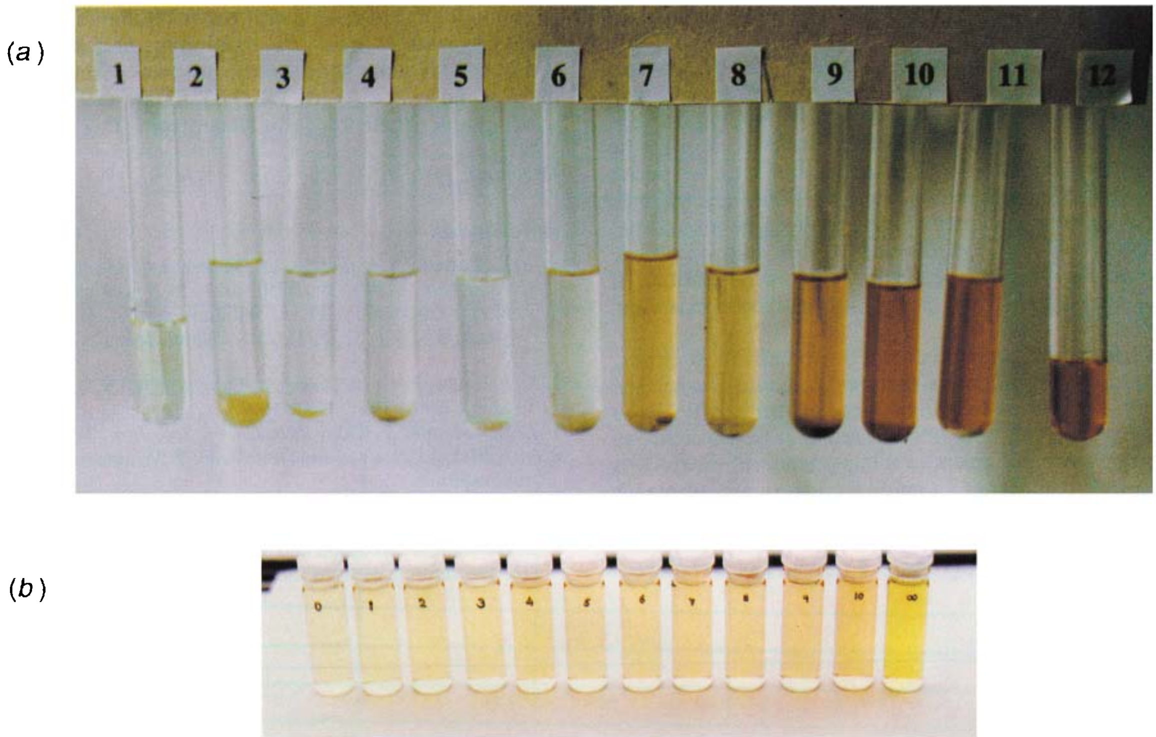


Fig. 1 Ferroin test solutions. (*a*) Test samples. The test tube numbers are identified in Table 1. (*b*) Colloidal silver samples used to determine the sensitivity of the ferroin test. The vials labelled n = 0–10 each contain 2.5 μmol Fe^{III}-ferroin and $n \times 0.02$ μmol Ag^0. The vial labelled ∞ contains 1 μmol Ag^0 and no Fe^{III}-ferroin.

Table 1 Results of the ferroin test. Ordering: increasing orange colouration proceeding down the column.

Sample number	Sample description	Observation
1	Fe^{III}-ferroin	Light yellowish green
2	$AgNO_3$	No indication of Fe^{III} reduction
3	Agox–sodalite untreated, white[a]	No indication of Fe^{III} reduction
4	Agox–sodalite 250 °C, green	No indication of Fe^{III} reduction
	NaAgox–sodalite 1 Ag/u.c., 2 h UV-hν	No indication of Fe^{III} reduction
	Agox–sodalite, 2 h UV-hν	No indication of Fe^{III} reduction
5	NaBr–sodalite	No indication of Fe^{III} reduction
	AgBr–sodalite, melt, untreated, sample A	No indication of Fe^{III} reduction
6	AgBr–sodalite, melt, untreated, sample B	Slight indication of reduction
7	AgBr–sodalite, aq. untreated	Some indication of reduction
	AgBr–sodalite, 150 °C, 1 h	Increasing indication of red
	AgBr–sodalite, 250 °C, 1 h	
8	AgBr–sodalite, 350 °C, 1 h	
9	AgBr–sodalite, 450 °C, 1 h	
	Agox–sodalite, 550 °C, 1 h	
10	H_2–Δ reduced AgBr–sodalite	
11	Ag powder	
12	Fe^{II}-ferroin	Orange

[a] ox = oxalate.

were added to test tubes containing a few mg of the test material and 5 ml distilled water. Each series contained a standard without silver and a standard of silver powder or colloidal silver. A reaction could be observed visually within a few hours. For greater sensitivity, UV spectra were obtained by diluting 200 μl of the test solution in a water-filled 1 cm quartz cuvette, using a cuvette filled only with water as reference. Absorption spectra of Fe^{II} containing species show maxima at 440, 480 and 510 nm. These bands are absent in solutions containing only Fe^{III} species.

The sensitivity of the ferroin test was determined by preparing a series of aqueous silver colloids (*ca.* 200 Å particle size) with known silver content. These were reacted with the freshly prepared ferroin(III) solution, using the same conditions as for the sodalite samples, and observing colour changes. Increasing amounts of an Ag^0 stock solution were added to eleven test tubes containing freshly prepared ferroin(III) solution. A definite colour change was observed for a solution containing at least 8.6 μg Ag^0. For 10 mg of a typical silver sodalite, this amount corresponds to *ca.* 0.2% external silver. The implication is that if the ferroin test is negative, *ca.* 99.8% of silver must have remained inside the sodalite framework. This observation is consistent with far-IR spectra[11] that show no significant reduction in the peak area corresponding to the Ag^+ translational mode after sample heating.

The colloidal silver solutions were prepared by mixing 20 ml of a chilled (ice bath) 1 mmol dm^{-3} aqueous $AgNO_3$ solution with 60 ml of a chilled 2 mmol dm^{-3} $NaBH_4$ solution in a darkened room. A yellow solution was formed immediately. For the first 60 min, the solution was shaken as soon as a red layer formed, owing to larger silver particles. The solution was allowed to stand for four days before use, in order to allow excess $NaBH_4$ to decompose. The mixture was diluted to 100 ml in a volumetric flask.

Fig. 1 shows photographs of the test solutions. The observations are summarized in Table 1. The test was positive for some, but not all, AgBr–sodalite samples. This indicated the possibility of some silver aggregation on the external surface of the sodalite crystals during the synthesis. The colour change was very small for a sodalite sample prepared by an $AgNO_3$ melt exchange, but was more significant when synthesized by an aqueous silver ion exchange at 150 °C. This was probably due to autoreduction of external Ag^+ ions with water in the hydrothermal reaction. Based on the increasing degrees of colour changes, the amount of external silver increased progressively upon heating the sodalite to 150, 250, 350 and 450 °C, and greatly upon reduction with hydrogen. These results agree with XPS (X-ray photoelectron spectroscopy) and XRD (X-ray diffraction) measurements.[11]

One might argue that ferroin could react with internal zero-valent silver *via* long range electron transfer by a tunnelling or hopping mechanism. Two experiments provide evidence that such mechanisms were negligible here. The first showed that the test was negative for UV irradiated or mildly heated silver oxalatosodalites, which contain internally confined silver clusters that were partially reduced by dissociative electron transfer of the imbibed oxalate anion.[5,6] The second showed that the optical plasmon absorption observed in heated AgBr–sodalite samples[11] which tested positively for silver by the ferroin test, could be removed by washing with sodium dichromate solution (1 g $Na_2Cr_2O_7$ in 100 ml distilled water, 1.5 days, room temp.).

The above experiments showed that the dark colour of heating silver halosodalites was largely due to external reduced silver agglomerates produced by autoreduction with occluded water (major) and perhaps framework oxygen (minor, since no change was observed in the ^{29}Si NMR).[11] Silver migration may have occurred through lattice oxygen defect sites created by autoreduction or through thermally expanded six-rings. By contrast, the colour changes observed for UV irradiated or gently thermalized silver oxalatosodalites[5,6] can be attributed to internally reduced silver clusters.

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