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METAL-CONTAINING CELLULOSE: SOME NOVEL MATERIALS

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ABSTRACT. This communication describes our preliminary studies of the preparation and characterisation of permeable cellulose films and filaments containing ca. 25% by weight metallic platinum, present as very small particles of colloidal dimensions dispersed throughout the cellulose matrix. The platinum (0)/cellulose displays high catalytic activity with respect to the decomposition of hydrogen peroxide.

1. INTRODUCTION

We have reported the preparation of small copper particles (3 to 30nm) dispersed throughout a permeable cellulose matrix[1]. The high loading (16% by weight metallic copper) means that the copper particles, while of colloidal dimensions, are far more closely packed than in conventional metal hydrosols.

An interesting feature of the copper(0)/cellulose is that particles of colloidal dimensions are easily accessible yet heterogeneous with respect to aqueous reaction mixtures. We were interested in extending our work to include the preparation of cellulose containing very small particles of the catalytically active noble metals; we describe here the preparation and properties of platinum-containing cellulose.

2. MATERIALS AND METHODS

Copper(0)/cellulose was prepared from solutions of cellulose dissolved in Cu/pn (a solution of copper(II) hydroxide in aqueous 1,3-diaminopropane[2]) as described previously[1].

Samples of copper(0)/cellulose, either washed but never dried or washed and dried, were immersed in ca. 0.1% by weight aqueous solutions of hexachloroplatinic(IV) acid of sufficient volume to ensure a large excess of platinum assuming that exchange occurred according to the equation:

$$2Cu(0)(cellulose) + Pt(IV) = 2Cu(II) + Pt(0)(cellulose)$$

Samples for spectroscopic examination were prepared by treating extremely thin copper(0)/cellulose films supported between Visking tubing (as described elsewhere[1]) with aqueous hexachloroplatinic(IV) acid; U.V./visible spectra were recorded on a Pye-Unicam SP8100 spectrophotometer.

The catalytic decomposition of hydrogen peroxide was monitored by measuring the evolution of oxygen with an electronic manometer. No attempt was made to maintain constant temperature in view of the vigour of the exothermic reaction, rather a temperature probe was employed to continuously record the temperature of the reaction mixture.

3. RESULTS AND DISCUSSION

Immersion of copper(0)/cellulose films or filaments in aqueous hexachloroplatinic(IV) acid resulted in an immediate darkening of the brown material; after ca. 20 minutes the platinum(0)/cellulose appeared almost black. The very thin samples sandwiched between Visking tubing were a transparent yellow-brown.

Three different reducing agents were used to prepare the copper(0)/cellulose films sandwiched between Visking tubing: sodium dithionite, hydrazine and sodium tetrahydridoborate(III) (all were 0.5 mol dm^{-3} in 1 mol dm^{-3} sodium hydroxide at 80°C). Spectral measurements (Figure 1) suggest that all reducing agents produce particles of the order 10 nm (undoubtedly a range of sizes as evidenced by our earlier transmission electronmicroscopic studies[1]) but that the average copper particle size increased with the following order of reducing agents under the conditions employed:

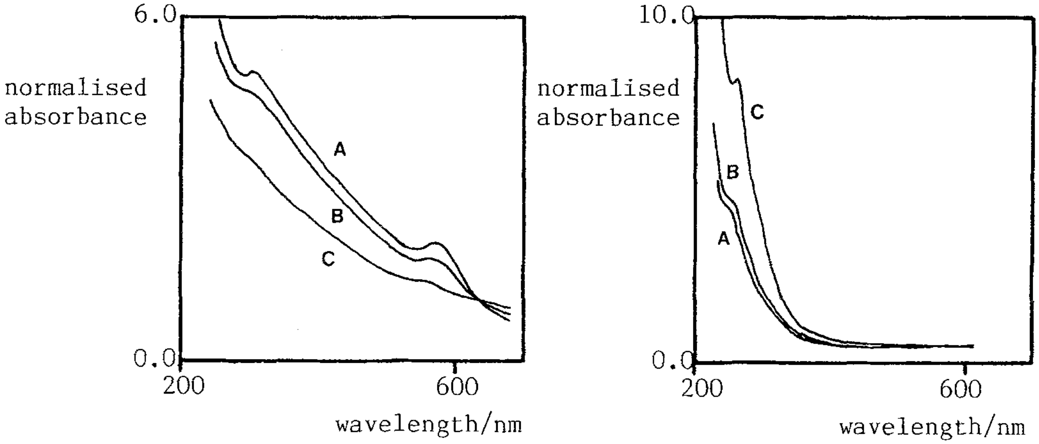
sodium tetrahydridoborate(III) < sodium dithionite < hydrazine

This may be related to two factors: the time required for the reduction to go to completion (sodium tetrahydridoborate(III) was the slowest reduction) and the rupturing of the cellulose structure by vigorously evolved nitrogen when hydrazine was used.

When these samples were exchanged with platinum the resulting sandwich films had very similar spectra to one another (Figure 2). The distinguishing feature of these spectra compared to that of a platinum sol (prepared in our laboratories by the citrate reduction method[3]) is the presence of a peak or shoulder at 250-300 nm. This feature was most prominent for films prepared from copper(0)/cellulose obtained by hydrazine reduction. The Mie theory suggests that the larger the platinum particles the greater should be the absorbance in this region[4] and this would be in accord with the pattern of particle sizes suggested for the copper(0)/cellulose precursors. At this stage a more detailed discussion of spectra is not warranted for the reasons outlined previously[1].

FIGURE 1

Absorption spectra of copper(0)/cellulose and platinum(0)/cellulose normalised at 650 nm and 450 nm respectively.

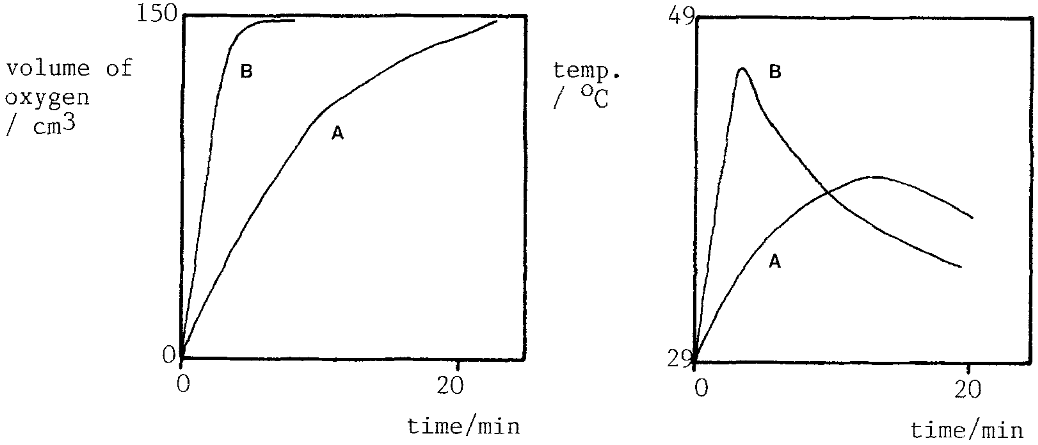


1.1 Cu(0)/cellulose; reducing agents: $A=NaBH_4$ $B=Na_2S_2O_4$ $C=N_2H_4$

1.2 Pt(0)/cellulose from Cu(0)/cellulose in 1.1

FIGURE 2

Rate of oxygen evolution and temperature rise during the catalysed decomposition of 10 cm^3 hydrogen peroxide (ca. 15 volume).



Catalysts used:
A: platinum hydrosol, B: ground, 'never-dried' platinum(0)/cellulose

Preliminary examination with a Philips 300 transmission electronmicroscope suggest platinum particles with overall dimensions of the order 5-50 nm but with a fine structure not apparent in the copper precursors: this might be anticipated in view of the probable growth pattern of the exchanging metal.

In order to assess the reactivity of the platinum(0)/cellulose, samples prepared by exchange with hydrazine reduced copper(0)/cellulose films, the catalytic decomposition of hydrogen peroxide was investigated. Comparison was made with a platinum sol prepared in our laboratories by the citrate reduction method (spectrum recorded above); in each case the number of moles of platinum atoms was the same. The catalysed decompositions were extremely vigorous and temperature control was difficult; therefore the temperature of the reacting mixture was monitored and this lent further evidence to the relative vigour of the catalysed reactions. All the platinum(0)/cellulose samples prepared in our laboratories were more effective than an equivalent amount of platinum sol. The most reactive platinum(0)/cellulose was obtained by exchanging a never-dried copper(0)/cellulose film with hexachloroplatinic(IV) acid, washing and grinding the product but not drying it prior to use. Results are shown in Figure 2. The extremely high reactivity of the platinum(0)/celluloses suggests high surface areas and this is as expected in view of the preparative method: crystal growth by exchange from parent copper particles of the order 3-30 nm in diameter.

We have described the preparation of a highly reactive form of platinum, small particles densely packed in a permeable cellulose support. Work is hand to characterise these materials more fully with respect to structure and catalytic activity. We hope to extend the work to other metals.

4. ACKNOWLEDGEMENTS

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5. REFERENCES

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