A STUDY OF THE PLATINIZATION OF SEMICONDUCTORS USING PHOTOACOUSTIC SPECTROSCOPY

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Summary

Platinized samples of tungsten trioxide, titanium dioxide and an ion exchange resin were examined by photoacoustic spectroscopy. For the oxide samples the lack of a simple relationship between signal intensity and loading was attributed to agglomeration–aggregation of the platinum on the surface of the oxide. The sample of platinized titanium dioxide having the maximum photocatalytic activity for methane production from acetic acid was found to have a relatively low loading (0.2 - 0.5 wt.%). The lower reactivity of the samples having a higher loading was attributed to the greater degree of agglomeration–aggregation of the platinum in these samples.

1. Introduction

The use of semiconductor catalysts in powder form doped [1] or platinized [2] is increasing as the search for catalysts capable of splitting water on irradiation with sunlight continues. The loading by precious metals may be optimized from the point of view of cost and of performance. The analysis of semiconductors loaded with precious metals requires non-destructive methods if any understanding of the surface morphology is to be gained. Recently the technique of photoacoustic spectroscopy (PAS) has been shown to be of value in studying the loading of dyes on fibres [3] and inert supports [4] and for mixtures of inorganic materials, *e.g.* potassium dichromate with magnesium oxide [5]. We now report on the use of PAS in an investigation of the loading of tungsten trioxide, titanium dioxide and an ion exchange resin with platinum. An attempt has been made to correlate these findings with the performance of the materials as catalysts for the photoinduced production of methane from acetic acid [6].

2. Experimental details

Tungsten trioxide (BDH; average particle size, 3 - 7 μm determined by transmission electron microscopy) and titanium dioxide (Degussa P-25;

average particle size, 300 Å determined by transmission electron microscopy) were platinized via the procedure developed by Tseung and coworkers [7]. A suspension of the oxide in an aqueous solution of potassium chloroplatinate (Hopkin and Williams) was sprayed as an aerosol into liquid nitrogen to produce rapid freezing of the mixture. This was followed by removal of the ice by application of a vacuum (10^{-3} Torr; 20 °C). The resultant mixture was reduced by hydrogen at 40 - 50 °C for 1 h. By varying the concentration of potassium chloroplatinate in the initial suspension, powders having various loadings of platinum were obtained.

The particle sizes of unplatinized and platinized samples of tungsten trioxide and titanium dioxide were measured in aqueous solution using a Malvern 2600/3600 particle sizer. Platinized and non-platinized tungsten trioxide samples were all found to have a particle size of 8.5 ± 1 μm. Similarly all the titanium dioxide samples were found to have a size of 7.25 ± 1.5 μm. Evidently dispersion of the oxides in water leads to agglomeration and consequently, whilst electron microscopy measurements are useful for characterizing materials, the results give little information as to the state of the materials when suspended in media such as water.

A polystyrene anionic exchange resin (CG 400; Sigma, 75 - 150 μm) containing quaternary ammonium groups was activated with aqueous sodium hydroxide and then platinized according to the method of Toshima *et al.* [8]. Each sample was shaken in aqueous chloroplatinic acid. This was followed by refluxing in aqueous ethanol (1:1 by volume) under nitrogen for 18.5 h and then by drying in air at 80 °C for 1 h.

Photoacoustic spectra were recorded on an EDT model OAS 400 instrument with a chopping frequency of 80 Hz.

X-ray fluorescence and transmission electron microscopy studies were carried out on a Jeol 100B microscope. Surface area measurements were made by nitrogen adsorption, utilizing a Micrometrics surface area analyser.

Irradiations were carried out using an 1800 W xenon lamp. The light was passed through a glass cell containing water (path length, 11 cm) to remove IR radiation and was focused on the front of the irradiation cell. The cell, of volume 27 cm^3, was filled with 20 cm^3 of reactant solution, consisting of 250 mg of catalyst in 10 vol.% aqueous acetic acid. Gas samples (200 μl) were removed from the cell at regular intervals and analysed on a Pye 104 gas chromatograph using a column of inside diameter 1/8 in packed with 5 Å molecular sieves at 100 °C. A thermal conductivity detector was employed.

3. Results

Figures 1, 2 and 3 show the photoacoustic spectra of platinized tungsten trioxide, titanium dioxide (80% anatase) and an ion exchange resin respectively. The band edges of the semiconductors can be clearly seen
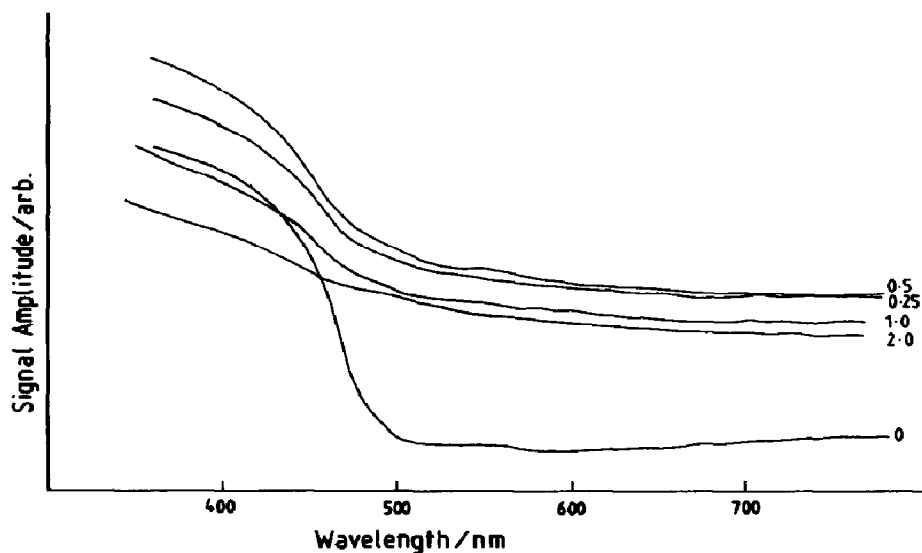
Fig. 1. PAS of platinized tungsten trioxide samples (modulation frequency, 80 Hz): numbers on curves refer to the weight per cent loading.
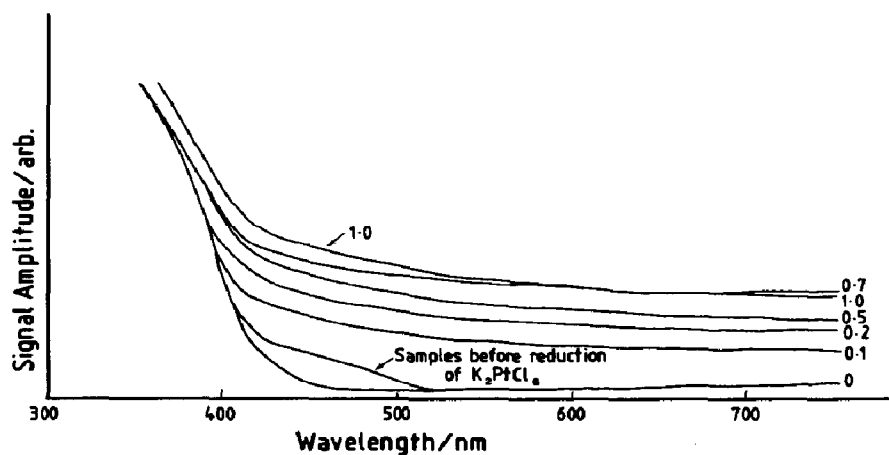

Fig. 2. PAS of platinized titanium dioxide samples (modulation frequency, 80 Hz): numbers on curves refer to the weight per cent loading.

in Figs. 1 and 2 [9]. The absorption which lies to the red of 450 nm is attributed to platinum.

In accord with this view, it can be seen from Fig. 2 that reduction of chloroplatinic acid gives rise to a species having an absorption band which extends from 400 nm out beyond 800 nm. Further confirmation that the particles were carrying platinum was obtained by X-ray fluorescence studies.

Figures 4 - 6 show the change in signal amplitude at 700 nm as a function of platinum loading. Figure 7 shows the yield of methane when argon-degassed aqueous acetic acid solutions of samples of platinized titanium dioxide were irradiated [6].
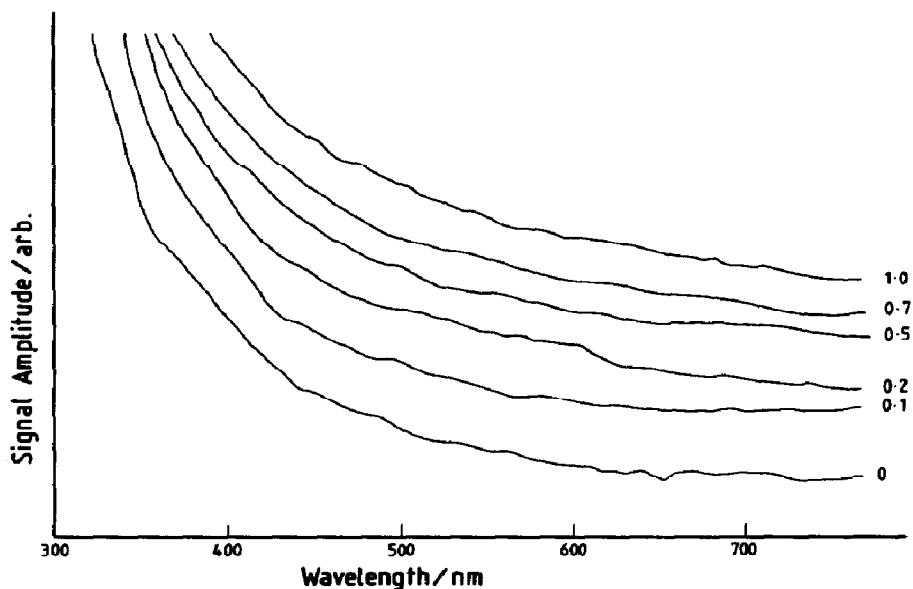
Fig. 3. PAS of platinized anion exchange resin samples (modulation frequency, 80 Hz): numbers on curves refer to the weight per cent loading.
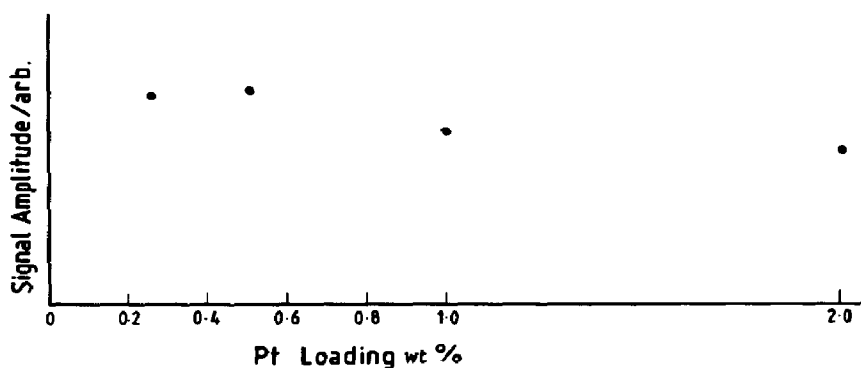

Fig. 4. Photoacoustic signal intensity as a function of platinum loading on tungsten trioxide (measured at 700 nm).

4. Discussion

The method of platinization utilized in this work was chosen because it is known that it leads to a high dispersibility and thus to a high surface area of the material deposited onto the support [7]. Furthermore, because the procedure uses relatively mild conditions, surface changes in the supports due to the heating (such as the strong metal support interaction) are unlikely to occur as a result of the deposition process. This is particularly important since surface area changes as well as agglomeration–aggregation of the particles could have a drastic effect on the photocatalytic performance of the materials. For the platinized titanium dioxide, all the samples, including
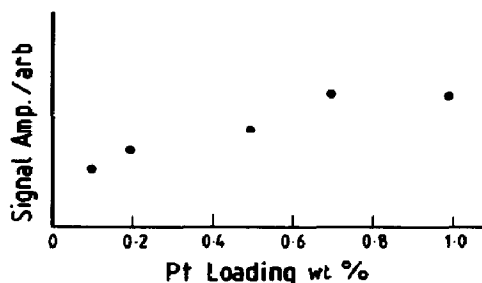
Fig. 5. Photoacoustic signal intensity as a function of platinum loading on titanium dioxide (measured at 700 nm).
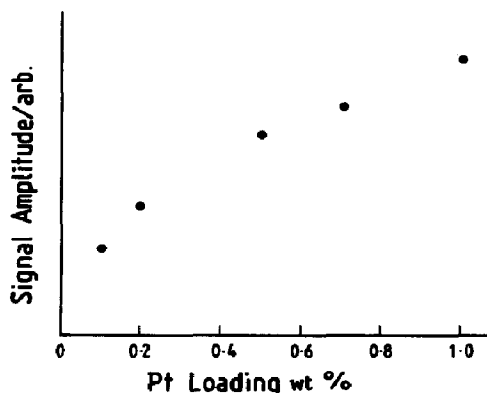
Fig. 6. Photoacoustic signal intensity as a function of platinum loading on an anion exchange resin (measured at 700 nm).

the non-platinized sample, had similar Brunauer–Emmett–Teller (BET) surface areas (about 42 m^2 g^{-1}), *i.e.* the platinization procedure and the platinum loading had little, if any, effect on the overall surface area of the titanium dioxide support.

The tungsten trioxide surface area was too low for accurate analysis by the BET method.

From Figs. 1 and 4 it can be seen that there is no obvious relationship between the PAS signal intensity due to the platinum and the loading. Matters are somewhat improved for platinized titanium dioxide (Figs. 2 and 5). At this point it is worthwhile to consider the origin of the photoacoustic signal [10]. Light absorbed by a sample, if not re-emitted as light, may give rise to a number of non-radiative processes and also produce heat. It is the production of heat that is measured in PAS. The amount of heat detected is determined by the physical nature of the sample, *e.g.* a sheet, crystals or powder, and in the case of a powder its particle size [11]. The optical properties of the material (extent of light penetration, and degree and nature of light scattering) are also very important. In the cases currently being considered, *e.g.* titanium dioxide, the particle size and surface areas of the sample of a particular oxide are similar. Thus the poor relationship between the PAS signal intensity and the loading cannot be attributed to changes in the radiative surface area of the oxides as a result of platinization. The root cause appears to be in the way in which the platinum is laid down on the surface of the oxide. It is possible that during the deposition process and subsequent treatment the platinum will aggregate on the surface of the oxide with the ultimate formation of islands of platinum. For a reasonable relationship between the PAS signal and the loading to be obtained it is necessary for the sample being probed (in this case platinum) not to be optically thick and also for the thermal diffusion length to be less than the optical path length. Since metal films are highly absorptive throughout the
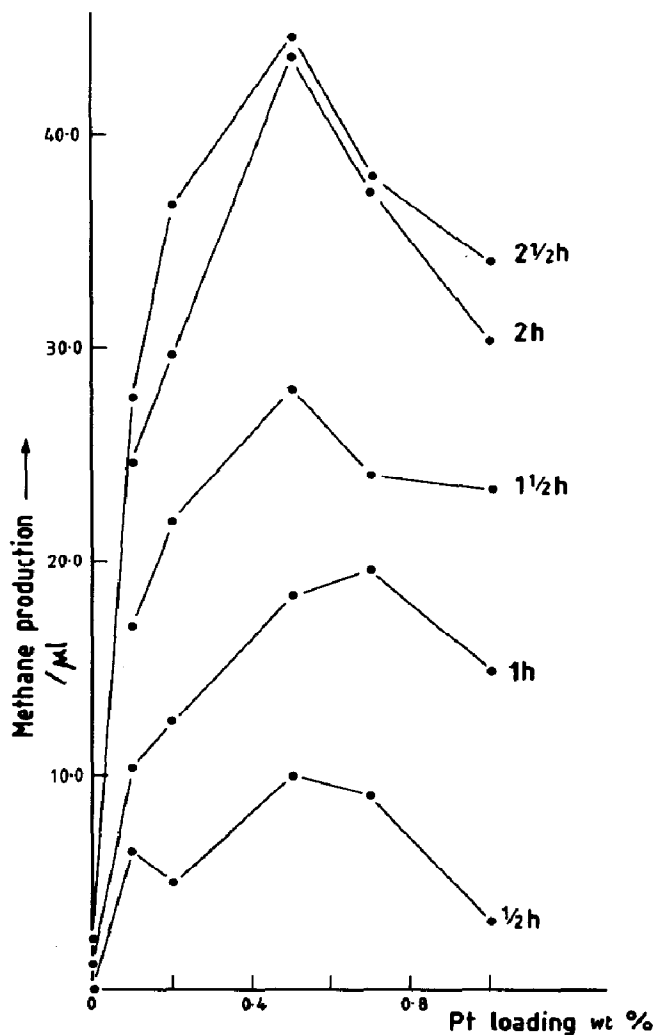
Fig. 7. Production of methane as a function of irradiation time and platinum loading for platinized titanium dioxide samples.

visible region, a reasonable relationship between the PAS signal and the loading will accrue only when the platinum is deposited onto the support surface in such a way that it is optically thin, *i.e.* if platinum particles are deposited they must be exceedingly small. If large particles are produced and the optical path length is less than the depth of the platinum to be penetrated then signal saturation will occur, *i.e.* as the optical thickness increases there will be no corresponding increase in the PAS signal intensity. Furthermore the presence of large particles or agglomerates on the surface of the oxide particles will provide both a heat sink and a heat-emitting site. A consequence of this is that a platinized sample of oxide will have different thermal radiative properties from those of a non-platinized sample and therefore the PAS signal of a platinized material will not only reflect in some measure the amount of platinum but also the modified thermal radiative

properties. For tungsten trioxide, optical saturation appears to be occurring at the 0.25 - 0.5 wt.% loading. For the 1 and 2 wt.% loadings the presence of platinum appears to be affecting the thermal properties of the material since the signal intensity decreases with an increase in the loading. Initial examination of these materials by transmission electron microscopy did not reveal the presence of distinct clusters of platinum. However, vigorous agitation of these samples in water produced materials in which the clusters separated from the semiconductor could be clearly seen by transmission electron microscopy. This finding suggests that at higher platinum loadings, and with supports of lower surface areas, aggregation of the platinum occurs. A reason for this may be the lack of suitable sites on the oxide surface to accommodate the platinum. (For the samples having a loading of less than 0.7 wt.%, agitation does not cause the release of any particles of platinum, suggesting that the adsorbed particles are firmly affixed and are not of a particularly large size.) The results for titanium dioxide shown in Fig. 2 suggest that the critical loading level is around 0.7 wt.%. The plot of signal intensity *versus* loading shown in Fig. 5 indicates that there is a better distribution of the platinum on the oxide than was obtained for tungsten trioxide partly due to the larger surface area of the support. However, the fact that the signal intensity does not increase to any large extent with increase in loading suggests that the platinum may be agglomerating although to a lesser extent than on tungsten trioxide. To check this point the platinization of the ion exchange resin was undertaken since with this system small particles of platinum should be produced at discrete sites. As can be seen from Fig. 6 the PAS signal intensity is far more sensitive to loading than for the oxide samples. The shape of the curve is far more akin to those obtained for reactive dyes on the surface of wool where it is known that aggregation is not a problem [3]. Recently Kiwi and Gratzel [12] have employed, with success, ion exchange techniques to platinize titanium dioxide. They have shown that the method used produces a far more even distribution of platinum on the surface of the oxide and the particles are very small.

To assess how the photocatalytic efficiency of the oxides varies with platinum loading the performance of platinized samples of titanium dioxide in aqueous acetic acid solution was examined. As can be seen from Fig. 7, the optimal loading for methane production is 0.5 wt.% Pt, and the 1 wt.% Pt loading is far less efficient. From the PAS spectra (Fig. 2) the 1 wt.% Pt loading appears to have some aggregated platinum since the signal for this sample at 700 nm is similar to that for the 0.7 wt.% loaded sample. The PAS spectra suggest that a 0.5 wt.% loading is optimal, indicating that small platinum particles are more efficient than larger particles in the photocatalytic production of methane.

5. Conclusion

The use of PAS to determine the level of loading of platinum on semiconductors is rendered difficult because the way in which the platinum

is laid down on the surface affects the signal intensity. The value of the technique lies in the fact that it gives a good indication of when the loading level becomes sufficiently high to cause agglomeration. This particular situation cannot always be readily resolved by microscopy.

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