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Analytical TEM Study of the Selective Photocatalytic Deposition of Platinum on Titania–Silica Mixtures and Silica-Supported Titania

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The photocatalytic deposition of platinum on titania was used to investigate the selectivity of the deposition of metal in the case of a multiphase support. Two kinds of supports were chosen: a mechanical mixture of TiO_2 and SiO_2 and a silica-supported titania. In both cases, the photodeposition of platinum corresponding to 1 wt% Pt was complete. For the mechanical mixture of TiO_2 and SiO_2, analytical transmission electron microscopy investigation revealed that platinum was deposited exclusively on titania. The chemical deposition of titania on spherical particles of silica gave small TiO_2 particles of 3–5 nm mean size. Raman spectroscopy indicated that deposited TiO_2 exhibits the anatase structure. As in the preceding case, platinum was photodeposited exclusively on supported titania particles. This was confirmed by TEM and EDX analyses. This method of metal deposition could be used to decorate a multicomponent support with a noble metal, the metal being exclusively deposited on the photosensitive parts or constituents. It represents a possible method of preparing a metal catalyst deposited on a highly divided supported support.

INTRODUCTION

When a semiconductor (SC) is put into contact with a solution containing a noble metal salt or complex and is illuminated with protons of suitable energy, i.e., greater than or equal to its band gap energy ($h\nu \geq E_G$), the metal can deposit as small crystallites, provided the redox potential be higher than the flat band potential of SC.

This phenomenon has been known for about 20 years (*1, 2*) and concerns various noble metals such as Pd (*3–13*), Pt (*7–9, 14–18*), Rh (*7, 8*), Au (*8, 19, 20*) and Ag (*1, 2, 21–27*) as well as various semiconductors, mainly oxides, such as ZnO, MoO_3, and predominantly TiO_2. These oxides can be present in the shape of single crystals, films, or powders. In addition to fundamental studies, devoted to the mechanistic aspect of the phenomenon, some possible applications can be mentioned.

First, this method can be envisaged as a means of precious metal recovery from (dilute) waste water. This has been proposed for Pt (*7, 8*), Au (*19*), or Ag (*27*).

Second, photocatalytic deposition can be applied to the synthesis, in mild conditions, of highly dispersed metal catalysts, either monometallic (*5, 6, 9, 16, 17*) or bimetallic (*9*).

In the present article, we shall study the selectivity of the photodeposition of a noble metal (Pt) in the case of a biphasic support containing only one photosensitive constituent.

Two kinds of support have been selected:

(i) a mechanical mixture of two oxides, and

(ii) a chemical deposit of one oxide on another.

For theoretical and practical reasons, discussed later, silica and titania were cho-

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sen as the best partners to manifest a possible selectivity in the photocatalytic deposition of the noble metal.

EXPERIMENTAL

1. Samples

The samples of silica and titania were prepared in a flame reactor according to Vergnon's methods (*28*). Si or Ti tetrachloride was vaporized and burnt in an oxyhydrogen flame, thus yielding practically homodispersed oxide particles, whose shape (spherical or polyhedral) and size could be controlled by adjusting the reactant flow rates and the temperature. Two nonporus samples of silica were selected: SiO_2 with a specific area of 85 $m^2\ g^{-1}$, corresponding to polyhedral grains of ca. 30 nm mean size; and SiO_2 (II) with a specific area of 51 $m^2\ g^{-1}$, in the form of spherical particles with a mean diameter of 50 nm.

A sample of titania (TiO_2 A), mainly anatase, was chosen for its spherical particles of ca. 65 nm diameter, corresponding to a specific area of 23.5 $m^2\ g^{-1}$. Degussa P-25 TiO_2 was taken as the reference (50 $m^2\ g^{-1}$; 80% anatase).

2. Photoreactor

The photodeposition was carried out in a static slurry photoreactor, previously used for this purpose (*7, 9, 27*). UV light penetrated the reactor through the bottom window, constituted by a pyrex optical disk which acts as a UV filter ($\lambda \geq 300$ nm). UV light was provided by a HPK 125-W Philips high-pressure mercury lamp. The suspension was permanently agitated with a magnetic stirrer prior to and during illumination.

3. TEM/STEM Analysis

Microanalytical studies were performed on an analytical transmission electron microscope (ATEM) Philips EM 420 equipped with a GATAN electron energy loss spectrometer and a silicon/lithium energy dispersive X-ray detector (EDAX).

The samples were first ultrasonically dispersed in isopropanol and a drop of this dispersion was deposited on a thin holey carbon film (200 Å thick) supported by a copper grid. The electron micrographs were obtained at 120 kV both in TEM and STEM modes.

RESULTS AND DISCUSSION

1. Selectivity of the Photodeposition of Platinum in a (TiO_2–SiO_2) Mechanical Mixture

1.1. Description of the TiO_2–SiO_2 Mixture

For an easy and unambiguous examination by electron microscopy of the metal deposit, the two oxides were selected with quite different textures: SiO_2 (I) with homodispersed polyhedral particles of ca. 30 nm mean size and TiO_2 (A) with spherical grains of ca. 65 nm diameter. The ratio R of the number n_1 of titania particles to that of silica, n_2, is given by the formula

$$R = \frac{n_1}{n_2} = \frac{m_1\rho_1^2 S_1^3}{m_2\rho_2^2 S_2^3} \qquad (1)$$

where m is the mass of each sample, ρ is the density, and S is the specific area, the subscripts 1 and 2 referring to TiO_2 and SiO_2 respectively. This expression is deduced from the formula $d = 6/\rho\ S$ which correlates the mean size d with ρ and S for homodispersed particles of either cubic or spherical shape. Specific areas and masses were chosen according to Eq. (1) to obtain a ratio R close to unity. This was achieved by preparing a mechanical mixture containing 65 mg of titania (23.5 $m^2\ g^{-1}$) and 5 mg of silica (85 $m^2\ g^{-1}$). Such a mixture gave a ratio R equal to $\approx$0.8 and enabled full light absorption by titania.

1.2. Photodeposition of Platinum

Both solids were suspended in 20 cm^3 of a solution of H_2PtCl_6 (1.8×10^{-4} *M*).

The slurry was stirred for 1.5 hr in the dark at room temperature to obtain a homogeneous mechanical mixture. No deposit of metal was observed but only a slight adsorption of H_2PtCl_6. The slurry was then illuminated for 10 min in the opened photoreactor. The solid was then centrifuged (13,000 rpm) and dried in an oven at 110°C for 4 hr. Initially white, the solid had become pale grey.

Platinum analysis of the supernatant solution by atomic absorption spectroscopy indicated that ca. 97% of chloroplatinic acid had decomposed and been reduced to metal according to the equation

$$PtCl_6^{2-} + 2H_2O \xrightarrow[h\nu]{TiO_2} Pt^0 + 6Cl^- + 4H^+ + O_2(g). \quad (2)$$

Equation (2) represents the overall reaction of the reduction of Pt^{IV} ions into metallic Pt atoms by the photoinduced electrons, whereas water is oxidized into oxygen by the photoproduced holes. The completion of reaction (2) is determined (i) by chemical analysis of the solution and of the solid and (ii) by measurement of the final pH of the solution. The stoichiometry of Eq. (2) is accounted for in Ref. (*7*). Platinum is present as small metal crystallites whose formation does not require further reduction by H_2.

The amount of photodeposited platinum corresponded to ca. 1 wt%.

1.3. TEM Study

The transmission electron micrographs and analytical data collected on the mechanical mixture are shown in Fig. 1. As expected, titania appears as crystalline spherical particles whereas silica is in the shape of amorphous contiguous grains.

The selectivity of the deposition process is illustrated by the transmission electron micrograph (Fig. 1) where Pt crystallites, of 1 to 2 nm in size, appearing as small dark points, are present only at the surface of the TiO_2 particles. This fact is confirmed by EDX spectra recorded on the two kinds of particles. The spectrum collected on several TiO_2 particles (Fig. 1) exhibits two characteristic peaks corresponding to titanium and platinum. In the case of a silica particle the spectrum presents only one peak relative to silicon.

The selectivity of photodeposition estimated from several other micrographs is 100% in favour of titania. The shape and the size of the Pt crystallites are identical to those obtained when TiO_2 alone is used (*7, 9*).

2. SELECTIVITY OF THE PHOTODEPOSITION OF PLATINUM ON SILICA-SUPPORTED TITANIA

2.1. Preparation of Silica-Supported Titania

For unambiguous TEM examination, a silica sample was chosen in the shape of nonporous spherical particles with mean diameter of 50 nm (SiO_2 II). SiO_2 (500 mg) was suspended in 50 cm^3 of dehydrated ethanol. Then, 57 mg of tetraethoxytitanium was added and stirred under static vacuum for 20 min before pumping. The rotovapor was subsequently heated to 50°C until the liquid phase had totally evaporated. The impregnated solid was then dried in an oven at 130°C for 4 hr, before being calcinated at 500°C for 8 hr under oxygen flow (12 dm^3 hr^{-1}) (heating rate: 1°C min^{-1}). The sample was finally cooled in oxygen to room temperature. The amount of deposited titania corresponded to 4 wt%.

2.2. Characterization of Silica-Supported Titania

2.1.1. Structure. The structure of silica-supported titania was identified by Raman spectroscopy using a Dilor multichannel spectrometer (OMARS 89) working with the 514.5-nm line of an Argon ion laser. The spectral slit width was 4 cm^{-1} and the spectra recording time was 80 sec.

The Raman spectrum of silica-supported titania is shown in Fig. 2 (curve A) and exhibits three bands at 396, 516, and 638 cm^{-1}, which are characteristic of anatase (*29*).

No peak relative to rutile could be detected. By comparison, the spectrum of

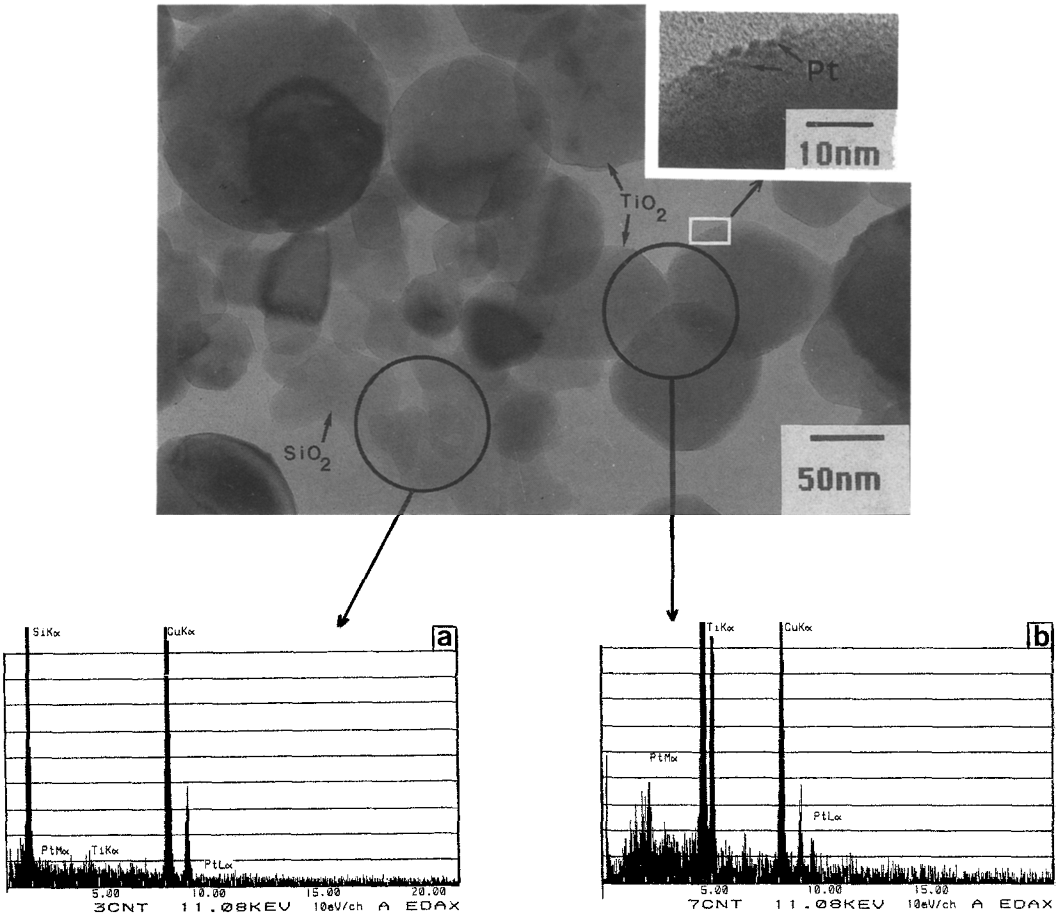

FIG. 1. Transmission electron micrograph and EDX spectra obtained with a 100-nm-diameter electron probe, from the Pt-decorated mechanical mixture (TiO_2 + SiO_2). (a) EDX spectrum of silica particles (only silicon $K\alpha$ X-ray is clearly visible); (b) EDX spectrum of TiO_2 particles showing the presence of platinum at their surface. The copper signal in both spectra is due to the copper support grid.

TiO_2 (Degussa-P25) was recorded under the same conditions (curve B). It shows the presence of a small peak at 450 cm^{-1}, indicative of the existence of a rutile phase in this sample. We can conclude that silica-deposited titania was constituted by pure anatase within the detection limits of LRS.

2.2.2. Texture. The anatase mixture was examined by TEM (Fig. 3). Supported TiO_2 is not present as a regular surface layer on silica but as small particles. Most of them have a diameter lying in the range 3–7 nm (Fig. 3). These particles are regularly distributed over all the grains of silica as shown in Fig. 4.

2.3. Photodeposition of Pt on (TiO_2)/SiO_2

Fifty milligrams of (TiO_2)/SiO_2 was suspended in 10 cm^3 of the H_2PtCl_6 solution necessary for the deposition of either 0.3 or 1 wt% Pt. The slurry was first agitated under pumping for 2 min, then under static vacuum for 10 min, and finally under a second pumping for 2 min. After such a procedure, the reactor was chromatographically oxygen-free.

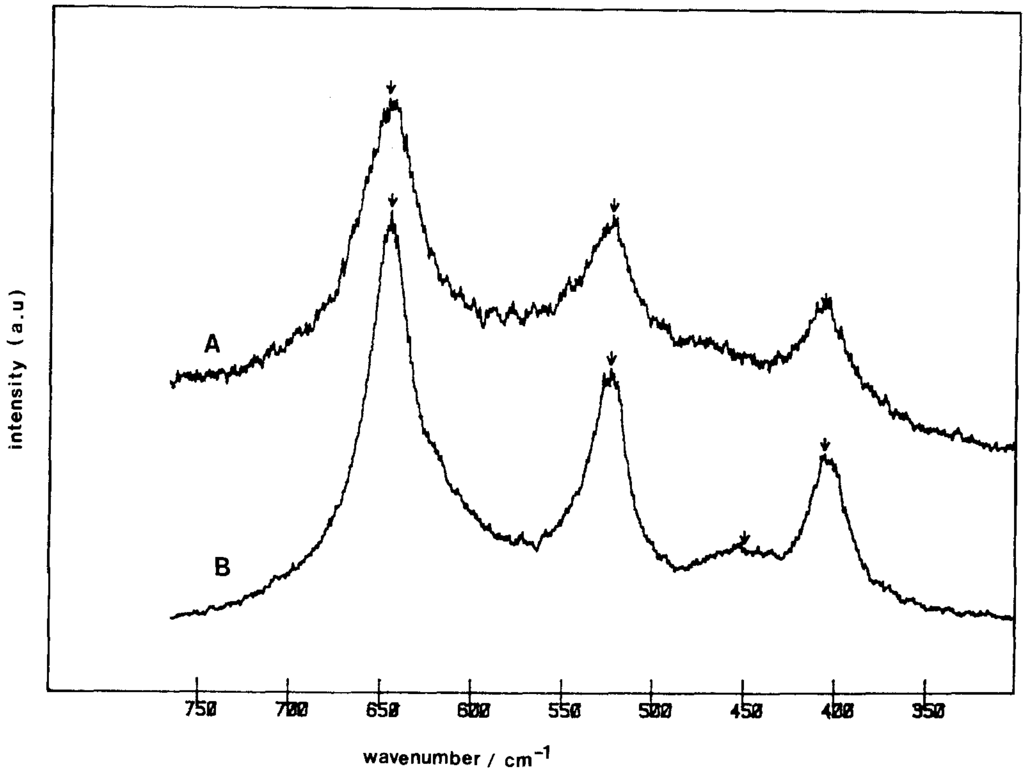

FIG. 2. Raman spectra of silica-supported titania (4 wt% TiO_2/SiO_2) (curve A) and of Degussa P-25 TiO_2 as a reference (curve B).

The solid was then illuminated for 15 min. After centrifugation at 13,000 rpm and washing with twice-distilled water, the solid was dried in an oven at 110°C.

Initially white, the solid had become pale grey. Analysis by atomic absorption spectroscopy of the supernatant solution indicated a 100% deposition of platinum.

2.4. *TEM and STEM Characterization of* $(Pt/TiO_2)/SiO_2$

TEM micrographs of $(Pt/TiO_2)/SiO_2$ are given in Fig. 5. Platinum particles appear as dark dots. Metal particles are generally agglomerated on particular points of the support. EDX analyses of the surface always indicate the simultaneous presence of Pt and Ti. This suggests that photodeposition always occurs on titania areas at the surface of silica.

Pt could not be seen on the very small deposits of TiO_2 because of the detection limits. Several particles of Pt were encountered on larger areas of titania. Pt photoreduction occurs according to the following equations:

$$h\nu + (TiO_2) \rightarrow e^- + p^+ \qquad (3)$$

$$(Pt^{IV}) + 4e^- \rightarrow Pt^0 \qquad (4)$$

$$nPt^0 \rightarrow Pt_n. \qquad (5)$$

It must be noted that the size of the Pt crystallites is similar to that deposited on unsupported titania (*9*). It is likely that this size of 1–1.5 nm is a characteristic of finely divided platinum.

CONCLUSION

The photocatalytic deposition of platinum on the titania–silica system is selec-

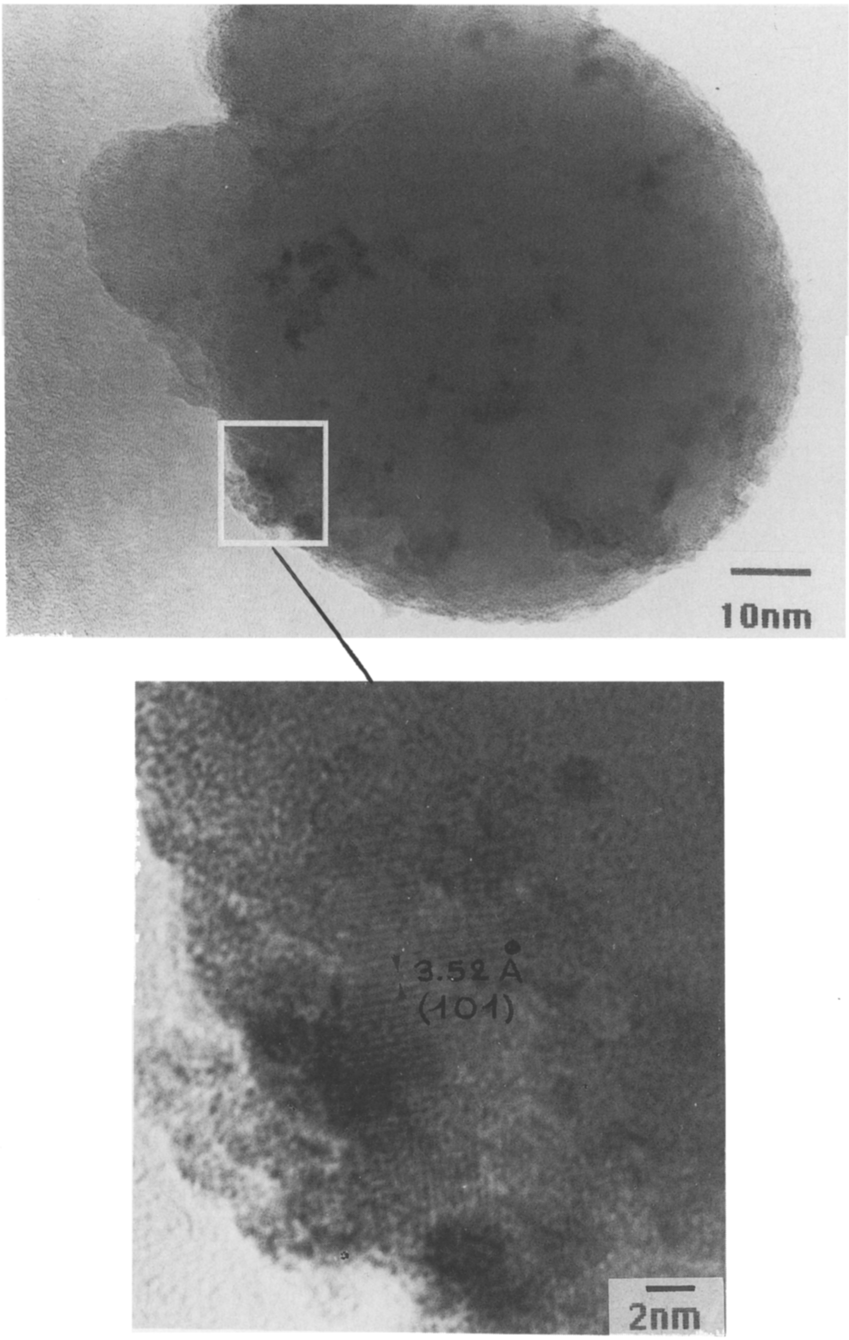

FIG. 3. Transmission electron micrograph of silica-supported titania. In the insert are shown the lattice fringes of anatase ((101) plane, 3.52-Å spacing).

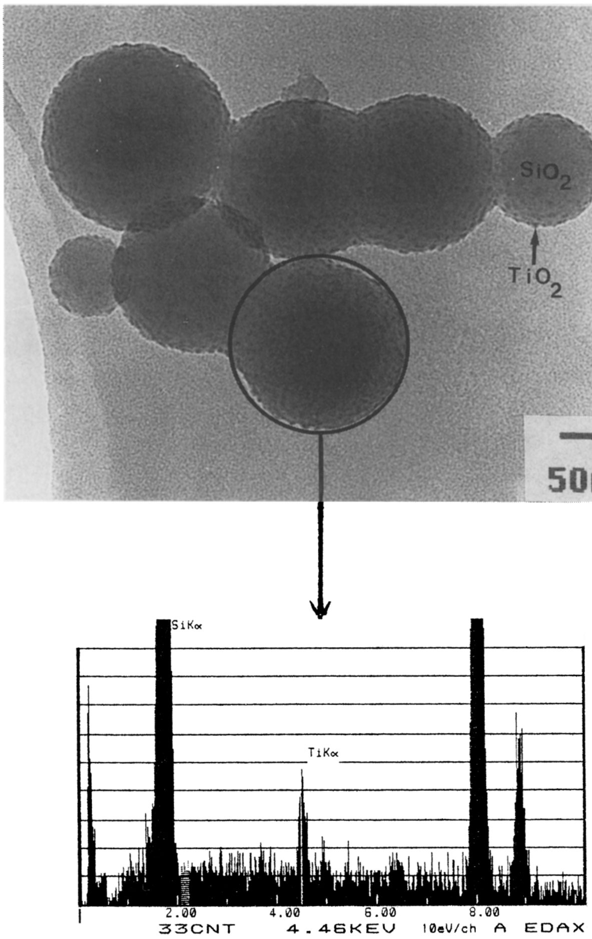

FIG. 4. Transmission electron micrograph of several spherical SiO_2 particles supporting small TiO_2 particles (3–5 nm diameter). Below, EDX spectrum of one SiO_2 particle showing the presence of deposited TiO_2.

tively orientated to the exclusive deposition of Pt on titania. The reason is due to the reduction of $PtCl_6^{2-}$ by photoelectrons induced by UV light in TiO_2. The presence of photodeposited platinum only on titania means that reduced Pt atoms cannot migrate from the surface of TiO_2 onto that of SiO_2. They spontaneously agglomerate into crystallites on the oxidic phase where the reducing photoelectrons have been generated.

The advantage of the method is that selective deposition of one metal on a particular phase or constituent of a preformed polyphasic support is possible.

In the case of silica-deposited titania, it has been shown that titania islands could be selectively decorated by photodeposited platinum. This could be of interest in preparing a metal catalyst deposited on a supported support.

This method of preparation could be extended to complex polyphasic supports, where the metal would selectively deposit onto their photosensitive constituents, which could be ZnO, CeO_2, Nb_2O_5, MoO_3, CdS, etc.

Finally, this method of preparation appears rather simple with only one period of reaction in a slurry reactor, at room tem-

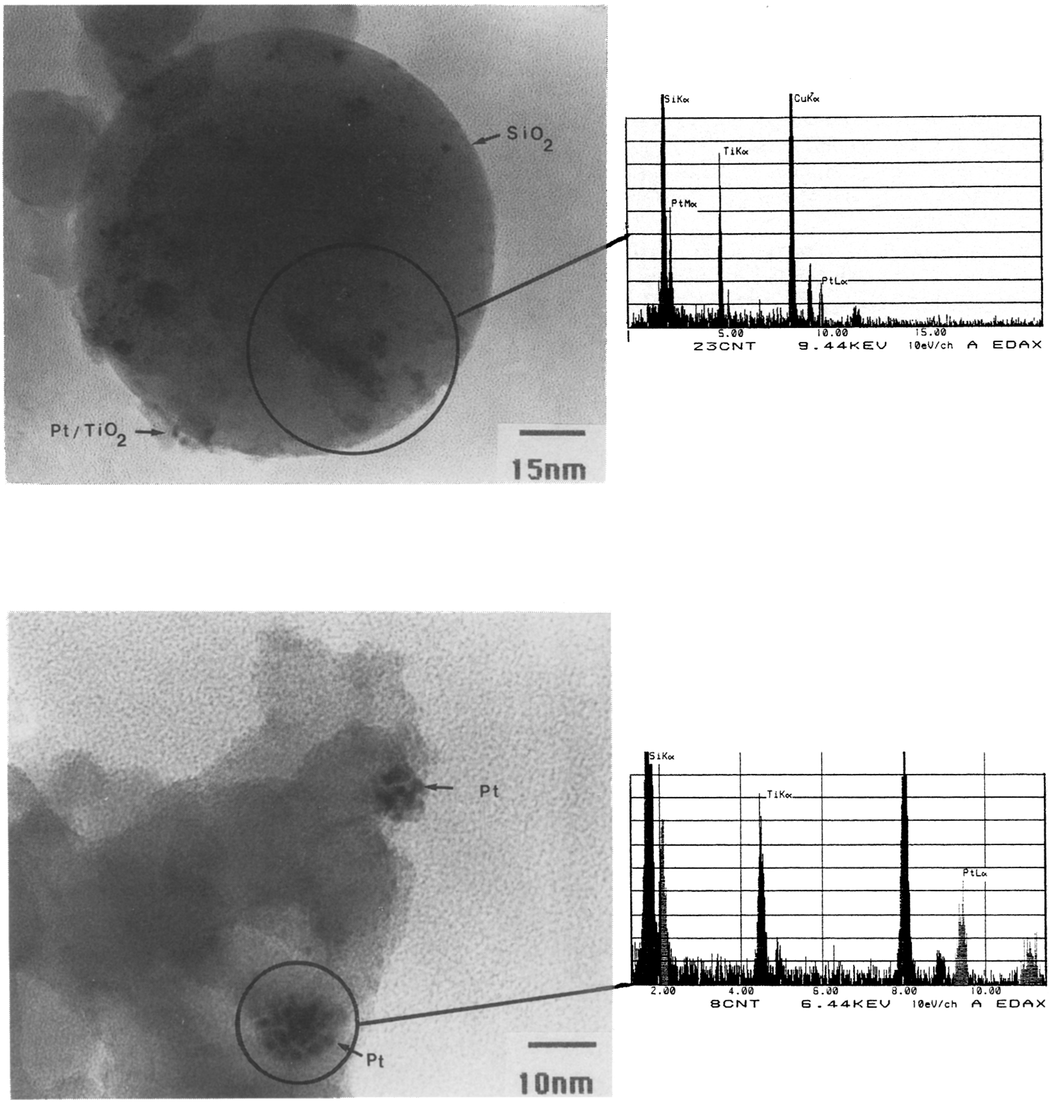

FIG. 5. Transmission electron micrographs and EDX spectra of (Pt/TiO_2) deposited on silica. The lower micrograph shows aggregates of several platinum crystallites (mean size: 1.5 nm).

perature, in the aqueous phase, without the necessity of using reducing agents such as hydrogen at high temperatures.

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