

THE CHARACTERIZATION AND BEHAVIOR OF CATALYSTS PREPARED BY HETEROGENEOUS PHOTODEPOSITION TECHNIQUES

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ABSTRACT. — Pt and Pd were deposited on TiO₂ substrates from an aqueous solution containing the metal salt and acetate by a photodeposition process. The characteristics of the catalysts were determined by scanning Auger and X-ray photoelectron spectroscopy and by X-ray diffraction techniques. The activity of these catalysts was compared for the solution phase hydrogenation of benzene with commercial Pt/Al₂O₃ and Pt black catalysts. The photo-oxidation of oxalic acid at metallized and non-metallized TiO₂ powders under oxygen-free conditions was also investigated. The results show the production of a soluble Ti(III) species and hydrogen production, which suggests that Ti(III) may be a surface intermediate in the photoreaction.

Introduction

Irradiated suspensions of semiconductor powders have been employed as photocatalysts for a number of solution redox processes^{1, 2}. The catalytic behavior of the powders is often significantly improved when the surface is partially platinized^{3, 4}. A method for the photodeposition of platinum on reduced TiO₂ powder was previously reported in a brief communication from this laboratory⁵. We report here the extension of this method to the preparation of Pt and Pd catalysts on TiO₂, WO₃, SnO₂, SrTiO₃, and Al₂O₃ supports, and an investigation of the physical properties of the resulting catalysts. We also compare the activity of the metallized catalysts for the hydrogenation of benzene to that of commercially available catalysts. The nature of the semiconductor photoreaction was probed by investigating the photo-oxidation of oxalic acid under oxygen-free conditions at bare and metallized TiO₂.

Experimental

MATERIALS AND APPARATUS

TiO₂ [99.9% anatase by X-ray diffraction; Matheson, Coleman, Bell (MCB)], WO₃ (Apache Chemicals), SnO₂ (MCB), SrTiO₃ (Atomergic Chimetals Corp., 99.9%), and Al₂O₃ (Fischer Scientific) powders were used as support materials. Reduced TiO₂ powders were prepared by heating them to 500°C in a hydrogen atmosphere for 2-3 hours. Pt/Al₂O₃ (5% MCB) and Pt black (MCB) were used for hydrogenation as received. H₂PtCl₆ solution was prepared from high purity Pt wire dissolved in aqua regia and contained 20 mg Pt/ml (0.01 M). PdCl₂ (MCB) was dissolved in HCl to form H₂PdCl₄, and contained 10.6 mg Pd/ml (0.01 M). Glacial acetic acid and Na₂CO₃ were of reagent grade. Spectroquality benzene and cyclohexene (MCB) were used for hydrogenation.

Experiments involving the photo-oxidation of oxalic acid employed either 1 g of the non-metallized TiO₂ or 0.25 g of the Pt/TiO₂ having a Pt content of 10% by weight. The reaction was carried out in a closed system fitted with a mercury manometer and two removable gas collection chambers. One gas chamber was closed to the system prior to illumination and served as a control; the second gas chamber remained open to the system during the photoreaction and contained the reaction products. The system was purged with a flow of purified N₂ for at least 2 hours prior to illumination and then sealed. Chromatographic analysis for H₂ was performed using a molecular sieve column coupled

to a flame ionization detector (Varian Aerograph, Model A700). Mass spectra were obtained on a Finnigan 2000 mass spectrometer. The presence of soluble Ti(III) in the product solution was indicated by formation of the yellow complex with oxalate. Quantitative analysis of soluble titanium involved oxidation to Ti(IV) with O₂ followed by spectrophotometric determination in a sulfate medium with peroxide⁵.

A 2500 W Xe lamp (Christie Corp., Model UF 30 KK) operated at 1600 W was used as the illumination source for catalyst preparation. The focused intensity was 4.5 W/cm². Long term photocatalytic experiments were conducted in an Atlas 6000 Weatherometer equipped with a 6000 W Xe lamp. Operated at 5400 W, the unfocused intensity was 40 mW/cm². Electron spectroscopy (ESCA and Auger) were performed on a Physical Electronics Model 540 instrument.

For hydrogenation a shaking machine with a thermostat controlled water bath (Eberbach Corp.) was used. Product analysis was performed using NMR spectra (Perkin Elmer, R12) and coupled GC-MS (Finnigan 2000 system). Surface area measurements were conducted on a Surface Area/Pore Volume Analyzer (Micrometrics Instrument Corp., Model 2100 D) using prepurified N₂.

CATALYST PREPARATION

For catalyst preparation 1 g of the powder was suspended in a mixture of 10 ml H₂PtCl₆ and 10 ml acetic acid. The pH was adjusted to the desired value (pH = 6) with Na₂CO₃. The system was purged with N₂ prior to illumination for removal of CO₂ and O₂, and the flow continued throughout the experiment. CO₂ produced during irradiation was collected in a saturated Ba(OH)₂ solution, and determined as BaCO₃. The Pyrex cell with a flat window for illumination was mounted in a water bath which served to remove IR radiation and which contained a water cooling coil to maintain constant temperature.

Following irradiation the powder was removed from the reaction mixture and washed with distilled water repeatedly, and then dried at 110°C for 14 hours.

All catalysts were stored under hydrogen in air-tight containers before use in hydrogenation experiments. The amount of Pt deposited on the TiO₂ powders was determined by weighing the powders before and after the photodeposition procedure. Numerous previous photocatalysis experiments^{3, 4, 6} have demonstrated that the TiO₂ powder is quantitatively recovered after such experiments.

Thermally produced Pt/TiO₂ catalysts were prepared by impregnating the TiO₂ powder by evaporation of measured aliquots of H₂PtCl₆, followed by reduction at 500°C under H₂ for 3 hours⁷. The powder was washed free of chloride ion and dried at 110°C under H₂ for 2 hours. The catalyst was stored, after drying, in an air-tight container under hydrogen.

HYDROGENATION

The thermal catalytic activity of the catalysts was compared by determining the rate of hydrogenation of benzene with the different Pt catalysts and the hydrogenation of cyclohexene by Pd catalysts. Solution phase hydrogenations⁸ were used to compare the photodeposited Pt/TiO₂ catalyst and commercially available Pt/Al₂O₃ and Pt black catalysts and were carried out under identical conditions of pressure, temperature, and mixing rate. Although photoreduced Pt catalysts showed activity for benzene hydrogenation at 30°C, 70°C was chosen as the standard temperature for catalyst comparison. A suspension of 400 mg supported catalyst in 30 ml of benzene was mounted on the shaking machine with the water bath held at 70°C. An oil manometer used to contain the hydrogen gas was adjusted manually to maintain a pressure of 1 atmosphere in the reaction cell. The hydrogenation was continued 3 hours, after which the extent of conversion was determined and the products analyzed by NMR (qualitative) and GC-MS (quantitative).

QUANTUM EFFICIENCY CALCULATIONS

To estimate the quantum efficiency of the deposition reaction, the light intensity of the xenon lamp was measured using a Scientech Power Meter (Model 361). The part of the total energy output absorbed by the TiO₂ slurry in a Pyrex cell (300 to 405 nm) was determined by integration of the Xe lamp spectrum, and corrected for the illumination area. The photon flux determined in this way is 6.6×10^{18} photons/s. From the Pt deposition rate for Pt in acetate media of 180 μmol/h (Table I) we calculate a quantum efficiency of ~ 1.8%.

Results and discussion

RATE OF METAL DEPOSITION

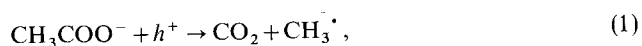
The photodeposition of Pt and Pd on semiconductor powders in acetate media proceeds by two paths: one involving a homogeneous reaction of the metal with acetate, and one involving heterogeneous catalysis at the semiconductor powder⁵. The data in Table I are the rates of Pt deposition with

Table I. — Comparison of heterogeneous and homogeneous Pt deposition rates^a.

Weight of TiO ₂ (g)	Volume H ₂ PtCl ₆ (ml)	Volume Acetic Acid (ml)	Dep. Rate (μmol/hr)
1.00	10	10	180.
—	10	10	50.
1.00	10	—	26.

^a All reactions at 55°C, pH 5.

and without the TiO₂ catalyst. The significant increase in reaction rate in the presence of catalyst shows that the heterogeneous process is more efficient⁹. The reduction is initiated when light energy larger than the semiconductor band gap (E_g) is absorbed by the particle, so that an electron-hole pair is formed. In acetate media, the possible oxidation reactions include³ acetate oxidation (the photo-Kolbe reaction):



and water oxidation:



The reduction process may involve reduction of protons or the metal species:



The pH dependence of the rate of photodeposition is illustrated in Table II. The rate is highest in the pH range 5–6, and falls significantly near pH 3. The ratio of the CO₂ evolution rate to the platinum deposition rate also exhibits a pH dependence. At pH 5, the ratio (Pt : CO₂) is in the range 1 : 1.8–2.2, whereas at pH 3 the ratio is 1 : 11.2. The results suggest that the reduction process which accompanies acetic acid oxidation involves two processes: one, the reduction of proton (leading to formation of methane), and secondly, the reduction of platinum on the particle surface. At pH 5, the kinetic factors favor platinum reduction, which results in a higher metal deposition rate. The fact that this ratio is lower than the stoichiometry predicted by equations (1) and (4), 1 : 4, suggests that water oxidation occurs as well (see Table I, experiment 3). Thus, Pt deposition by the photoelectrosynthetic (thermodynamically uphill) route in the absence of acetate is also possible, although at a lower efficiency. Similar results were previously reported for Cu deposition on TiO₂¹⁰.

Table II. — pH dependence on Pt deposition rate.

Deposition Rate^a

pH	(μmol/hr)
0	00.0
3	17.0
4	17.8
5	18.4
6	18.0

^a 1.00 g TiO₂, 25 ml solution volume 50% acetic acid, 0.05 M H₂PtCl₆; pH adjustment with Na₂CO₃.

In Table III the deposition rates are given for different metal-support combinations. The reaction rate was higher with reduced TiO₂ than on unreduced powder, which is consistent with results of the photo-Kolbe reaction³. The heterogeneous reaction also occurred readily at WO₃ ($E_g = 2.8$ eV), SnO₂ ($E_g = 3.5$ eV), and SrTiO₃ ($E_g = 3.2$ eV). ZnO undergoes photodissolution in the reaction mixture at pH 6. The deposition, presumably via the homogeneous photocatalytic mechanism, proceeds on Al₂O₃ ($E_g > 7$ eV), but the rate is much smaller than at a semiconductor powder.

HYDROGENATION REACTIONS

Platinum catalysts produced in the photoreduction process were compared to commercial catalysts on the basis of their activity for benzene hydrogenation (Table IV). Although liquid phase hydrogenation is more complex than the gas phase reaction⁸, the results provide a convenient means of comparing the catalysts. Because they have a larger surface area, the Al₂O₃ catalysts showed an overall higher activity than an equal weight of the other supported catalysts. The TiO₂ catalyst produced by the photoreduction method showed higher activity than a

Table III. — Photodeposition rates for various metal support combinations ^a.

Metal	(g) Catalyst	T ± 2(°C)	t (hr)	Deposition Rate (μmol/hr)	% Metal ^b Deposition
Pt	1.30 TiO ₂ (<i>a, r</i>) ^c	55	5.3	180	13.0
Pt	1.00 TiO ₂ (<i>a, u</i>) ^d	55	5.5	163	9.2
Pd	1.00 TiO ₂ (<i>a, r</i>)	55	3.8	280	17.1
Pt	1.00 WO ₃	55	5.0	82	7.7
Pt	1.00 Al ₂ O ₃	55	5.0	38	3.6
Pt	1.01 TiO ₂ (<i>a, u</i>)	40	24.0	35	14.0
Pt	1.01 SrTiO ₃	40	24.0	17	6.8
Pt	1.00 SnO ₂	40	24.0	33	13.4

^a All reactions pH 5.^b g metal/g powder X 100.^c (*a, r*)=anatase, reduced (*see* experimental section).^d (*a, u*)=anatase, unreduced.**Table IV.** — Hydrogenation of benzene, 70°C ^a at different supported Pt catalysts.

Support Material	Surf. Area (m ² /g)	%Pt (by wt.)	Conversion (%)	Time (hr)	Rate (mmol/hr)	Minimum Turnover ^b Number
TiO ₂ (<i>a, u</i>)	15	9.1	4.2	4.5	2.10	50.0
TiO ₂ (<i>a, r</i>)	15	12.8	4.0	3.0	4.10	47.0
TiO ₂ (<i>a, r</i>) ^c	15	7.0	1.5	3.0	1.50	31.0
WO ₃	13	7.7	4.8	4.0	2.70	69.0
Al ₂ O ₃	137	4.4	4.3	3.0	3.20	107.0
Al ₂ O ₃ ^d	>160	5.0	7.2	3.0	5.40	56.0
— ^e	10	100	9.0	3.0	6.80	20.0

^a T = 70°C, 400 mg catalyst.^b Turnover = mmol cyclohexane formed/mmol-Pt; this calculation assumes that all Pt atoms are available for reduction of benzene.^c Thermally produced, *see* experimental section.^d MCB, 5% catalyst.^e Pt Black, MCB.

similar catalyst produced thermally in this laboratory. Note, however, that thermal reduction of Pt on TiO₂ produces strong metal-support interaction ¹¹ which may reduce the activity of the catalyst for benzene hydrogenation ¹². Although the present experiments did not optimize the procedure for thermal Pt reduction, a comparison to the photodeposited Pt catalysts is provided by experiments with Pt Black, Pt/Al₂O₃ (MCB), and the thermally prepared Pt/TiO₂. In the case of Pt/WO₃ the reaction mixture turned a deep blue upon the addition of H₂. This color change can be attributed to the formation of tungsten bronzes, H_xWO₃ and indicates the ready formation of atomic hydrogen at the surface ¹³.

The Pd/TiO₂ catalyst showed no activity for benzene hydrogenation under these conditions. However, 400 mg of the palladium catalyst (7.8% Pd) reduced cyclohexene to cyclohexane at a rate of 2.8 mmol/hr at 70°C.

PHOTO-OXIDATION OF ACETATE AND OXALATE

The long term stability of the supported catalysts as photocatalysts was investigated using the photo-Kolbe reaction in 5 M acetic acid. The rate of CO₂ evolution as a

function of illumination time is given in Figure 1. The total turnover number, expressed as moles CO₂ produced per mole Pt, in the experiment was 319 in 425 hours at an intensity of 40 mW/cm². These platinized catalysts show enhanced activity for the photocatalytic decomposition of acetate ³ and oxalate, as compared to the non-platinized powders (Table V).

Some insight into the chemical nature of the semiconductor reaction was provided by the studies of oxidation of oxalic acid at TiO₂ under oxygen-free conditions. In this oxidation process, no hydrocarbon radical is generated by oxalic acid to scavenge hydrogen atoms from the particle surface so that more H₂ is generated than in the acetic acid oxidations (Table V). The process is slow at non-metallized TiO₂, but photodecomposition of oxalic acid proceeds at both the reduced and unreduced anatase catalysts, producing CO₂ and H₂. Moreover, during the decomposition at metal-free catalyst the solution turns perceptibly yellow. This was shown to be a complex ion of Ti(III) and oxalate by spectrophotometry, and the total yield of soluble titanium was determined by oxidation and measurement of the solution absorbance of the peroxy complex ⁵ (Table V). On the Pt/TiO₂, however, no soluble titanium species was found.

Table V. — Oxidation rates at platinized and non-platinized TiO₂ photocatalysts ^a.

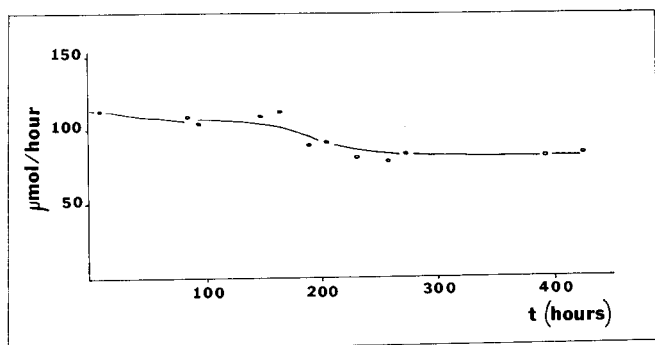
Catalyst	CO ₂ Evol. Rate (μmol/h)	H ₂ Evol. Rate (μmol/h)	Ti ³⁺ Reduc. Rate (μmol/h)
A. Acetic acid (5 M), oxygen-free conditions			
TiO ₂ (a, r) ^b	59	0.0	0.0
Pt/TiO ₂	360	18.0	0.0
B. Oxalic acid (1 M), oxygen-free conditions			
TiO ₂ (a, u) ^c	26.5	6.0	10.2
TiO ₂ (a, r)	63.8	24.5	11.9
Pt, TiO ₂	583	97.5	0.0
C. Oxalic acid, oxygen-saturated conditions ^d			
TiO ₂ (a, r)	310	0.0	0.0
Pt/TiO ₂	1330	0.0	0.0

^a 2500 W xenon lamp; 30 ml solution volume; all Pt/TiO₂ experiments use 250 mg. of 10% catalyst; all TiO₂ experiments use 1.0 g.

^b (a, r)=anatase, reduced; see experimental section.

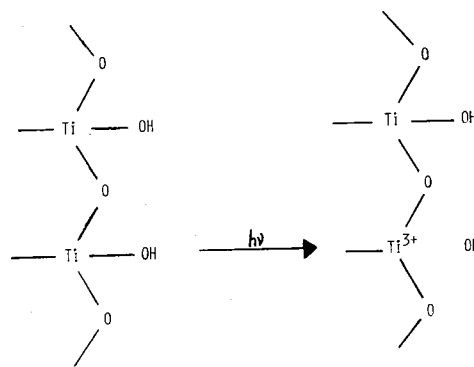
^c (a, u)=anatase, unreduced; see experimental section.

^d Reaction cell continuously purged with O₂.

**Figure 1.** — The rate of CO₂ evolution for the photo-Kolbe reaction at 40°C for 200 mg Pt/TiO₂ in 50 ml 5 M acetic acid under oxygen free conditions.

The presence of soluble titanium in these experiments provides a possible chemical model of the photoprocess at the TiO₂ particle. Irradiation produces an electron-hole pair. Spin-trapping experiments¹⁴ have shown production of OH[•], probably by reaction of the hole with a surface hydroxyl ion. The electron could then be trapped at a Ti(IV) site, leading to production of a Ti(III) species. The process is illustrated in Figure 2. In the presence of Pt, the reaction between Ti(III) and H⁺ is catalyzed. In its absence the electronic charge remains for some time leading to the negative charging of the TiO₂ particles as found in recent photoelectrophoresis experiments¹⁵. Oxalate ion, which is known to coordinate with Ti(III), is effective in dissolving this species. This model thus provides a rather simple chemical picture of the surface trapped hole and electron.

In oxygen-saturated solutions, oxalic acid oxidation is enhanced by the reduction of O₂, which occurs readily at the powder (Table V, entry C). Under these conditions, either surface Ti³⁺ sites would be oxidized by O₂ or adsorbed O₂ provides the site of a trapped electron (producing O₂⁻). In both cases no Ti(III) species would be detected in solution.

**Figure 2.** — Schematic representation of the photochemical reaction at TiO₂.

PHYSICAL CHARACTERIZATION OF CATALYSTS

Analysis of the prepared catalysts was conducted by electron spectroscopy (Auger and XPS) to determine their purity and to investigate the oxidation state of the deposited metals. Platinum catalysts showed signals at 75.4 eV (4f^{5/2}) and 71.85 eV (4f^{7/2}) consistent with a zero valent Pt¹⁶. The Pd catalyst also appeared to be zero valent 340.9 eV (3d_{3/2}); 335.7 eV (3d_{5/2}). Scanning Auger spectroscopy was used to determine the surface coverage of Pt on TiO₂. Mapping of the surface for Pt (45 eV), Ti (387 eV), and O (510 eV) showed an apparent uniform coverage by the Pt with a 0.4 μm beam. No evidence of isolated clusters or islands was seen. Higher magnification resulted in a loss of resolution due to a large charging current on the TiO₂.

X-ray powder diffraction measurements showed no peaks in the 2θ regions where the primary diffraction peaks for Pt and Pd are expected. This was demonstrated by S. J. Tauster *et al.*¹¹ to be consistent with Pt crystallites less than 25 nm in size. No agglomeration of the metal on the powder surface was detected. The X-ray diffraction analysis, however, does reveal a partial conversion to rutile structure in the TiO₂ powders reduced at 500°C.

Surface area measurements for TiO₂ were consistently in the range of 13 to 15 m²/g before and after deposition, so that no measurable increase in area occurred with the reduction of the metal.

Conclusions

The results reported here confirm our previous communication⁵ that metal photodeposition methods on semiconductor or insulator substrates are useful in the preparation of catalysts. The advantage of this method is that deposition occurs at or near the sites of photoexcitation and this promotes high dispersion. The low temperature at which the process is carried out probably also reduces surface diffusion and agglomeration of the reduced metal. The enhanced activity of the platinized powders for photoprocesses has been discussed previously^{1, 3, 4} and can be attributed to enhancement of the reduction process by the Pt site. This prevents a build-up of electrons in the semiconductor particle which would shift the particle potential in a negative direction and increase the rate of recombination with holes. The results support the view that

irradiated photocatalysts are a convenient method of producing highly oxidizing conditions (e. g. Pt/TiO₂ as a hydroxyl radical source) in aqueous solutions. Further applications and investigations of such materials are in progress.

Acknowledgment

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