ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 113 (1998) 181–188

Journal of Photochemistry and Photobiology A:Chemistry

Influence of metallic silver and of platinum–silver bimetallic deposits on the photocatalytic activity of titania (anatase and rutile) in organic and aqueous media

Antonino Sclafani [a,*], Jean-Marie Herrmann [b]

[a] Dipartimento di Ingegneria Chimica dei Processi e dei Materiali, Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy

[b] Photocatalyse, Catalyse et Environnement, Ecole Centrale de Lyon, BP 163, 69131 Ecully Cédex, France

Received 3 November 1997

Abstract

The influence of deposited silver upon the photocatalytic activity of titania in the rutile and anatase allotropic forms has been studied in three different reactions. The common feature found for these three reactions was an electron transfer from illuminated TiO_2 to silver particles. In the first reaction (platinum photodeposition), it has been shown that the initial presence of metallic silver orientates the localization of subsequent Pt photodeposits with, in particular, a 100% selectivity to Pt deposition on top of silver particles or agglomerates previously deposited on anatase. In the second reaction (2-propanol oxidation), Ag deposit was found beneficial for the activity of rutile and detrimental for that of anatase. For rutile which is less active, silver helps for the electron-hole pair dissociation. By contrast, for anatase, the negatively charged Ag particles preferentially attract photoholes and become recombination centers, thus decreasing the photocatalytic activity. For the third reaction (dehydrogenation of 2-propanol), Ag/TiO_2 catalysts were found very poorly active, as expected for a group I-B metal. However, in the additional presence of platinum deposits, $Pt/Ag/TiO_2$ catalysts are as active as their Pt/TiO_2 homologues, thus confirming that Pt is deposited on top of silver with good electronic contacts between both metals. The three photocatalytic reactions have common electronic processes based on the photoelectron generation on titania and the subsequent electron transfer to the metal(s). © 1998 Elsevier Science S.A.

Keywords: Photocatalytic activity; Platinum photodeposition; Rutile; Anatase

---

1. Introduction

Heterogeneous photocatalysis is based on the photonic activation process, which enables it to work at room temperature. Several reaction media can be used: gas, liquid, or aqueous phase. In the latter case, one can cite many examples of water detoxification by pollutant degradation [1–3], whereas gas and liquid phase reactions are mostly concerned with oxidation reactions [4–6].

An efficient photocatalyst is a solid which harmoniously combines good chemisorptive and photoelectronic properties, which confer to it good aptitudes (i) to absorb efficient photons; (ii) to generate electron-hole pairs and (iii) to separate them with a minimum of recombination. Most photosensitive solids are chalcogenides like sulfides (CdS, MoS_2, ZnS) or oxides (TiO_2, ZnO, Fe_2O_3, WO_3, ZrO_2, etc.), but the best photocatalyst remains titania (Ref. [3] and references therein). Brookite, rutile and anatase are three natural allotropic forms but anatase has been permanently found as the most efficient form in photocatalysis [7–11].

Several attempts have been performed to increase the photoactivity of titania: addition of photosensitizers, ion-doping or metal deposition. In the latter case, a deposit of (noble) metals such as Pt, Pd, Rh or Ni has been found beneficial only for reactions involving hydrogen either as a reactant (alkane–deuterium isotopic exchange [12–14]) or as a reaction product (alcohol dehydrogenation [15]).

In photocatalytic oxidations, according to Wang et al. [16], the reaction rate is controlled by charge-transfer to O_2. The presence of group VIII metals deposited over the semiconductor catalyst improves the charge-transfer rate to O_2 [17,18] and consequently the photo-oxidation of the organic compounds becomes more efficient. This behavior has been previously observed by other authors using single crystal [19] and polycrystalline [20,21] TiO_2 doped with Pt or Pd [22]. Moreover it has been also observed that a significant increase of the photo-oxidation rate of 2-propanol occurs only

---

[*] Corresponding author.

1010-6030/98/$19.00 © 1998 Elsevier Science S.A. All rights reserved

PII S1010-6030(97)00319-5

for low amounts of Pt (or Ag) and that the optimum amount of metals depends on the physico–chemical characteristics of TiO_2 used and on the reaction medium [23]. The above behavior appears to be general since a critical amount of metal is needed also in other cases [16,24] in order to obtain a photocatalyst with a maximum activity.

Nevertheless, it has been reported [25] that Pt/TiO_2 is less active than neat TiO_2 for the photocatalytic oxidation of liquid cyclohexane in the presence of air. A similar behavior was observed [26] by using the same catalysts, i.e., Pt/TiO_2 and TiO_2, for the photocatalytic oxidation of 4-chlorophenol in water. These contradictory results are probably due to the type of TiO_2 utilised, to the reaction medium, to the nature of the redox processes, to the metal content and dispersion.

The objectives of depositing metals over semiconductor catalysts are to improve the electron-hole pair separation and also to increase the rate of the reduction process due to the catalytic properties of the metal itself. Most of the deposited (noble) metals that have been previously studied belonged to group VIII. Very few studies concerned silver deposits [24]. In the present work, the influence of deposited silver over anatase or rutile has been followed in three different types of reactions: (i) metal deposition, (ii) oxidation and (iii) dehydrogenation. The final solids obtained in the first type of reaction ($Pt/Ag/TiO_2$) were also used as catalysts in the two other test reactions to make a comparison with TiO_2 and Ag/TiO_2. The same reactant (2-propanol) was chosen because (i) it gives a good stoichiometry in dehydrogenation (H_2/acetone ≈ 1) with negligible secondary reactions due to a relative stability of the acetone produced [15], and (ii) its photocatalytic oxidation has been selected as a test-reaction to evaluate the photocatalytic inertness of TiO_2-based pigments and their consequent resistance to chalking and weathering when exposed to atmospheric conditions [27,28]. Recently a note [29] has been published on this topic.

2. Experimental

2.1. Materials

The photocatalysts used were samples containing either rutile (Tioxide 1601/2; specific area = 20 m^2/g) or anatase (Tioxide 1601/1; specific area = 14 m^2/g) or both allotropic forms (Degussa P-25, specific area = 50 m^2/g; mainly anatase (ca. 70%) with non porous particles).

To prepare the initial Ag/TiO_2 samples [30], 500 mg of TiO_2 were suspended in 100 ml of an aqueous solution of $AgNO_3$ (Merck) of the desired concentration to get a final catalyst containing 0.5% Ag. The dispersion was deaerated with a rotatory pump for 15 min before UV-illumination, which was maintained for 16 h to make sure that all silver was photodeposited. The suspension was than centrifuged. The solid was repeatedly washed and then dried in an oven at 353 K. The amounts of silver deposited were determined by chemical analysis of the solid.

2.2. Photocatalytic experiments: apparatus and procedures

The photocatalytic reactions of isopropanol mild oxidation and dehydrogenation were performed in a batch photoreactor. The static photoreactor was a cylindrical flask of ca. 90 ml with a bottom optical window of ca. 4 cm in diameter transmitting light with $\lambda > 300$ nm. It was connected to a rotatory pump or to gas chromatographs. A volume of 10 cm^3 of liquid phase was used. Illumination was provided by a Philips HPK 125-W high-pressure mercury lamp. A 2.2-cm-thick circulating-water cell was placed in front of it to absorb the IR radiation. The radiant flux entering the reactor was measured with a calibrated radiometer (United Technology, model 21 A). Unless otherwise indicated, it was equal to 50 mW cm^{-2}, corresponding to a flux of efficient photons directly absorbable by TiO_2 equal to 4.18×10^{16} photons cm^{-2} s^{-1}.

The quantity of TiO_2 was chosen equal to 50 mg (sufficient to absorb the incident light flux) [15] and dispersed in 10 cm^3 of aqueous 2-propanol ($C_0 = 0.5$ mol/l). During the photocatalytic tests, these dispersions were magnetically stirred.

The photocatalytic oxidation was performed with aerated suspensions. Since the initial rate is constant for at least 2 h, a reaction time of 90 min was chosen to compare the different photocatalysts. After this illumination period, the suspensions were centrifuged and the supernatant liquid was analyzed by GC (Intersmat IGC type 20 chromatograph, equipped with a Hallcomid MH 15% on Chromosorb PA W 60–80 mesh column).

The same conditions were used for 2-propanol photodehydrogenation. The dispersions were initially briefly deaerated using a rotatory pump until no oxygen was detected by on-line gas chromatography. The formation of hydrogen under illumination was monitored by gas chromatography (Intersmat catharometer using a 2 m Porapak Q column and nitrogen as carrier gas).

3. Results and discussion

3.1. Photocatalytic photodeposition of platinum on Ag/TiO_2

3.1.1. TEM and STEM analyses

The photocatalytic deposition of platinum on titania samples (anatase and rutile) and on titania-deposited silver samples (Ag/TiO_2) was performed in the same type of photoreactors as that used in photocatalytic dehydrogenation. A final weight percentage of 0.5% was chosen for both Ag and Pt. The initial support was impregnated first in the dark in 10 cm^3 of an aqueous solution containing the total amount of platinum desired and prepared from a commercial solution of $H_2PtCl_6 \cdot 6H_2O$ (Merck) containing 3.9 wt.% Pt. The same procedure as for Ag photodeposition was used and to make sure that all platinum was deposited, the illumination was maintained for 16 h. The $Pt/Ag/TiO_2$ anatase and rutile samples were then washed several times and dried in an oven at 353 K.

These solids were then examined by transmission electron microscopy (TEM) using a JEOL 100 C microscope. Scanning transmission electron microscopy for STEM-EDX analyses was performed with a STEM field-emission gun (VGHB 50 I) equipped with a silicon–lithium diode detector (Link) and a multichannel analyzer (Tracor 5500). The samples were dispersed by sonication in ethanol and deposited on a carbon film supported on a copper grid.

After photodeposition of a low amount of silver (0.5 wt.%), small Ag particles could be observed on the anatase sample as in Ref. [30]. By contrast a different distribution of metallic Ag over rutile was observed and no metallic silver could be detected by TEM on most of the rutile particles. This was due to a very poor dispersion of silver on rutile.

After photodeposition of 0.5 wt.% Pt on both types of titania (neat TiO_2 and Ag/TiO_2), some particles of nanometric size were detected, which were ascribed to platinum crystallites. For the Ag/TiO_2 supports, STEM-EDX analyses permanently indicated the presence of platinum when silver was present. However, on Ag/TiO_2 rutile, platinum could also be found alone without the presence of silver and was under the shape of small dots at the periphery of rutile particles. By contrast, for Ag/TiO_2 anatase after photodeposition of Pt, platinum was never found alone, but always in the presence of silver. The local STEM-EDX analyses of spots, where small metallic particles ($1 \leq d \leq 2$ nm) were present, indicated that both silver and platinum were present with comparable atomic percentages. For larger metallic agglomerates, silver had an atomic percentage several times larger than that of platinum. In addition, the metallic composition within the large agglomerates was not constant. These observations indicated that platinum has been deposited as small crystallites on top of larger ones constituted by previously photodeposited silver. There was a 100% selectivity for platinum photodeposition on silver particles although chloroplatinic acid initially adsorbs on all the surface of anatase.

3.1.2. Electronic origin of the selectivity of platinum photodeposition on silver particles

The photocatalytic deposition of platinum Pt^{IV} obeys the following stoichiometry [31]:

$$(Pt^{IV})^{4+} + H_2O \xrightarrow{TiO_2 + h\nu} Pt^{\circ} + 4H^+ + O_2(g) \qquad (1)$$

The agglomeration of Pt atoms into crystallites was proposed to occur via two alternative mechanisms [30,31].

(1) Spontaneous agglomeration of Pt atoms into clusters and then into crystallites according to:

$$mPt^{\circ} \rightarrow Pt_m \qquad (2)$$

(2) Reduction as a cathodic-like process at small metallic nuclei

$$Pt^{\circ} + Pt^{4+} \rightarrow Pt_2^{4+} \xrightarrow{+4e^-} Pt_2^{\circ} \xrightarrow{Pt^{4+}} Pt_3^{4+} \xrightarrow{+4e} Pt_3^{\circ} \rightarrow \dots \rightarrow Pt_m \qquad (3)$$

The same mechanisms were later proposed for silver [30], the initial metallic nuclei being potentially able to correspond to the latent image made of Ag clusters involved in the photographic process.

To better choose between both mechanisms, a recent study has been performed using in situ EXAFS experiments [21]. For technical reasons, gold (Au^{III}) was chosen since it can be photodeposited even in an acidic medium, which is necessary for the colloidal state of titania required by the in situ EXAFS analyses [32]. It was clearly demonstrated that the second mechanism was most likely since a negative electrical charge enrichment of the initially formed gold particles occurred in agreement with a surprisingly low intensity of the threshold feature at the Au LIII edge [32].

In the present study, the electron enrichment of initially present Ag particles occurs spontaneously:

$$(TiO_2) + h\nu \rightarrow e^- + h^+ \qquad (4)$$

$$e^- + (Ag) \rightarrow e^-(Ag) \qquad (5)$$

in agreement with previous studies [33–36].

The spontaneous photoelectron transfer to Ag particles convert them into small cathodes at the surface of which the photoreduction and the subsequent photodeposition of platinum readily occur,

$$4e^-(Ag) + (Pt^{IV})^{4+} \rightarrow Pt^{\circ}/Ag \qquad (6)$$

The same process continues even when all the silver particles are covered with platinum in electronic contact with Ag. The electron transfer from illuminated titania to silver (and to platinum) is thermodynamically possible since the Fermi level of illuminated titania is higher than that of silver (and of platinum). Actually, illuminated titania behaves, from the electronic point of view, as a partially reduced TiO_2 and favors electron transfer to the noble metal [37–40].

Although the photocatalytic deposition of platinum follows the same mechanism on both types of titania, the behavior of anatase is slightly different from that of rutile. On anatase, the photodeposition of Pt takes place exclusively on previously photodeposited Ag particles with a 100% selectivity, whereas, on rutile, Pt deposits can be encountered either on top of silver or on rutile as small particles agglomerates.

Besides a possible difference in electron mobility in anatase and rutile, the difference in selectivity for local photodeposition of platinum can be mainly explained by the poor dispersion of silver on rutile. TEM and STEM examinations of Ag/TiO_2 (rutile) have shown that most of silver deposits were concentrated in a small number of large particles. This means that large areas of rutile, including entire rutile particles, do not support any silver and are not in contact with a metal particle. This situation reduces the probability of an easy transfer to silver for electrons photogenerated on these areas of particles. Chemisorbed Pt^{IV} complexes can therefore be more easily reduced as Pt° deposits without any connection with silver.

On the contrary for anatase, since the dispersion of silver is larger, most of anatase particles are in interaction with at least one particle of silver on which Pt photodeposition readily occurs via Eqs. (4)–(6).

3.2. Photocatalytic oxidation of 2-propanol to acetone

The influence of Ag, Pt and of Pt–Ag deposits on the photoxidation activities of anatase and rutile was determined by comparing their reaction rates with those of neat titania samples (Table 1). The last column clearly indicates that neat rutile is about three times less active than neat anatase. However rutile and anatase have opposite behaviours in the presence of one or two metals: for rutile, metal deposits are beneficial, whereas for anatase they are in general detrimental (Table 1). These results are in agreement with previous studies [7,8].

$$\text{Rutile} < 0.5\%\ \text{Ag/Rutile} < 0.5\%\ \text{Pt}/0.5\%\ \text{Ag/Rutile} < 0.5\%\ \text{Pt/Rutile}$$

$$\text{Anatase} > 0.5\%\ \text{Pt/Anatase} > 0.5\%\ \text{Ag/Anatase} > 0.5\%\ \text{Pt}/0.5\%\ \text{Ag/Anatase}$$

In the case of anatase, these results confirm the previous ones obtained on Pt/TiO_2 in oxidation reactions, either in pure liquid organic phase [25] or in water solutions [7–9,41]. In the present reaction, a deposit of 0.5 wt.% Pt made on anatase Degussa P-25 for comparison produced a decrease in photocatalytic activity from 4.0×10^{-4} to 3.13×10^{-4} mol/h. This decrease is limited but significant.

The detrimental effect on photoactivity of the subsequent deposition of Pt on Ag/anatase (Tioxide) was confirmed by results obtained with another commercial anatase sample (anatase BDH (British Drug House)): the photoactivity decreased from 1.74×10^{-4} mol/h for 0.5% Ag/anatase (BDH) to 1.5×10^{-4} mol/h for 0.5% Pt/0.5% Ag/anatase (BDH).

This detrimental effect can be ascribed to electron processes. In aqueous phase, the oxidation of 2-propanol involves OH° radicals generated by photoinduced holes h^+ [42,43]:

$$(H_2O)+h^+ \rightarrow OH^\circ + H^+ \tag{7}$$

$$CH_3\text{-CHOH-}CH_3 + OH^\circ \rightarrow H_2O + CH_3\text{-}C^\circ OH\text{-}CH_3 \tag{8}$$

The photoelectrons are trapped by chemisorbed oxygen:

$$O_2(g)+e^- \rightarrow O^-_{2(ads)} \tag{9}$$

which can then react with protons to form HO_2°

$$O^-_{2(ads)} + H^+ \rightarrow HO_2^\circ \tag{10}$$

HO_2° radicals can react either with 2-propyl radicals to form acetone:

$$HO_2^\circ + CH_3\text{-}C^\circ OH\text{-}CH_3 \rightarrow H_2O_2 + CH_3\text{-CO-}CH_3 \tag{11}$$

or with other HO_2° radicals:

$$HO_2^\circ + HO_2^\circ \rightarrow H_2O_2 + O_2 \tag{12}$$

In both cases, the hydrogen peroxide spontaneously formed decomposes in contact with illuminated titania, thus forming additional OH° radicals which contribute to the initial step of 2-propanol oxidation by H-abstration (Eq. (8)). In the presence of a deposited noble metal such as Pt, there is a spontaneous electron transfer from the illuminated support to the metal. This is due to the alignment of the Fermi levels of both phases. Such a reaction has been confirmed by photoconductivity measurements performed in vacuo [44].

The electron transfer was shown to persist under oxygen atmosphere [45]. This means that less electrons are available for oxygen ionosorption at the surface of titania (Eq. (9)), as confirmed by oxygen chemisorption [45]. As a consequence, for oxidation reactions, not only fewer $O^-_{2(ads)}$ species are formed because of the electron transfer to the metal, but also some photogenerated positive holes are attracted by negatively charged metal particles, which become recombination centers:

$$h^+ + e^-(\text{metal}) \rightarrow N + \text{energy} \tag{13}$$

where N represents a neutral center. The energy produced is released as heat. It can be easily conceived that if two metals

Table 1
Photocatalytic activities of naked titania samples and of Ag- and Pt/Ag-containing samples in the mild oxidation of aqueous 2-propanol to acetone

Support	Catalyst	Photocatalytic activity in mol of acetone produced per h (mol/h)
Rutile (TiO_2 (R) Tioxide)	TiO_2 (R)	1.3×10^{-4}
	0.5% Ag/TiO_2 (R)	2.7×10^{-4}
	0.5% Pt/TiO_2 (R)	4.7×10^{-4}
	0.5% Pt/0.5% Ag/TiO_2 (R)	2.9×10^{-4}
Anatase (TiO_2 (A) Tioxide)	TiO_2 (A)	3.5×10^{-4}
	0.5% Ag/TiO_2 (A)	3.0×10^{-4}
	0.5% Pt/TiO_2 (A)	3.2×10^{-4}
	0.5% Pt/0.5% Ag/TiO_2 (A)	2.9×10^{-4}

$C_0 = 0.5$ mol/l; light flux = 50 mW/cm^2; $m = 50$ mg TiO_2; $t_{UV} = 90$ min.

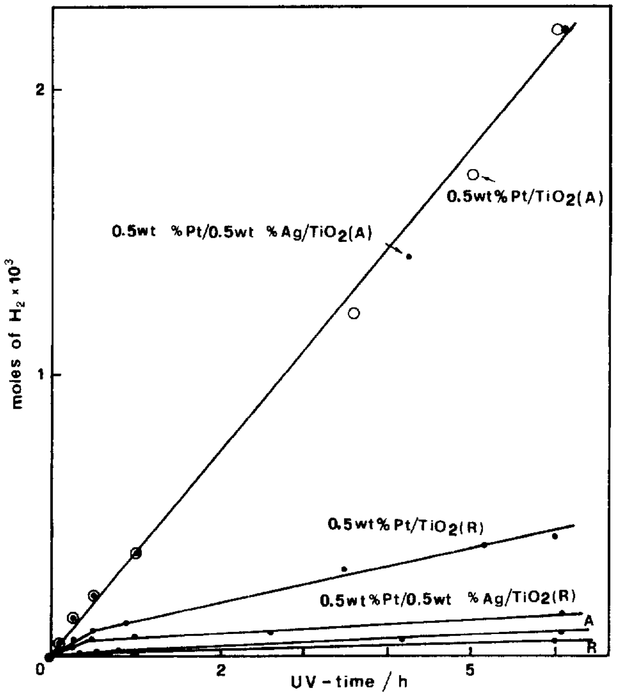

Fig. 1. Kinetics of hydrogen production in 2-propanol dehydrogenation performed in contact with Ag, Pt and Pt–Ag metal catalysts deposited on anatase TiO_2 (A) and rutile TiO_2 (R). The two lower curves (A) and (R) refer to 0.5 wt.% Ag deposited on anatase and rutile, respectively.

are present, the electron transfer from the support to the metal is more important and the inhibition of the reaction more pronounced.

By contrast, the effect observed on rutile is the opposite: the deposition of 0.5 wt.% silver increases the activity in 2-propanol oxidation and the addition of 0.5 wt.% Pt strengthens the beneficial effect observed. In that case, the same electron transfer to metal described above for anatase remains valid. However, it should be considered that the beneficial effects are preponderant. Rutile is intrinsically less efficient than anatase (Table 1, column 3). This could be ascribed (i) to less efficient adsorptive properties with respect to the oxygen and (ii) to a higher rate of electron-hole recombination [46].

In the case of rutile, the electron transfer to the metal will help the electron-hole pair dissociation and the separation of the opposite charges, thus favoring the photocatalytic process. Moreover, O_2 reduction on deposited metal is more efficient than in pure rutile from a kinetic point of view. In line with this proposal, it can be observed from the data of Table 1 that after metal depositions, rutile's activity is promoted to a level which is comparable to that corresponding to the activity of anatase. The beneficial effect of a metal deposit for rutile and the detrimental one for anatase is in agreement with previous results obtained by Tanaka et al. [7] and Rivera et al. [8].

The data of this work, together with others reported in the literature tend to indicate that, in contrast with Gerischer's previsions [16–18], O_2 reduction over TiO_2 anatase is not always under charge transfer control. The presence of a metal, even belonging to group VIII, and being catalytically active in O_2 reduction, cannot improve the kinetics of this reduction. As previously explained and with regard to anatase properties such as its superficial hydroxylation degree [47,48] and to the amount of metal deposit, the photocatalytic activity in oxygen reduction as well as in the whole oxidative process, can also decrease.

3.3. Photocatalytic dehydrogenation of 2-propanol

The same catalysts were used in the photocatalytic dehydrogenation of 2-propanol.

$$CH_3\text{-}CHOH\text{-}CH_3 \rightarrow CH_3\text{-}CO\text{-}CH_3 + H_2 \qquad (14)$$

This reaction is typical of illuminated titania-deposited (noble) metal catalysts (Pt, Pd, Rh, Ni) [15,39]. The stoichiometry of this reaction has been already established as well as the reaction mechanism [15,39]. The different reaction rates based on the hydrogen production ($r = dn_{(H_2)}/dt$) were calculated from the slopes of the straight lines of Fig. 1. The total numbers of mol of acetone and hydrogen produced after 6 h of UV-illumination are given in Table 2.

It is first confirmed that anatase is much more photoactive than rutile. The ratio of the number of mol of acetone produced in 6 h by 0.5 wt.% Ag deposited on anatase to that produced by 0.5 wt.% Ag deposited on rutile is equal to 4.2, i.e., identical to the ratio of that produced by 0.5 wt.% Pt/anatase and 0.5 wt.% Pt/rutile, (Table 2, column 2). Secondly, it is also confirmed that silver is a very poor (de)-

Table 2
Quantities of acetone and hydrogen (in mol) produced during 6 h of UV-illumination of 50 mg catalyst suspended in 10 cm^3 of aqueous solution of 2-propanol (0.5 mol/l)

Photocatalyst	Number of mol of acetone produced during 6 h	Number of mol of hydrogen produced during 6 h
0.5% Ag/TiO_2 (R)	8.2×10^{-6}	5.0×10^{-5}
0.5% Pt/TiO_2 (R)	4.2×10^{-4}	4.2×10^{-4}
0.5% Pt/0.5% Ag/TiO_2 (R)	1.1×10^{-4}	1.9×10^{-4}
0.5% Ag/TiO_2 (A)	3.4×10^{-5}	8.0×10^{-5}
0.5% Pt/TiO_2 (A)	1.7×10^{-3}	2.2×10^{-3}
0.5% Pt/0.5% Ag/TiO_2 (A)	1.7×10^{-3}	2.2×10^{-3}
0.5% Pt/TiO_2-D	1.9×10^{-3}	2.3×10^{-3}

hydrogenation metal co-catalyst, when compared to platinum. The same ratio of relative photoactivities (Pt/Ag) was obtained whatever the nature of the titania support (Table 2, column 2):

$$\frac{0.5\%\ \mathrm{Pt/anatase}}{0.5\%\ \mathrm{Ag/anatase}} = 50 = \frac{0.5\%\ \mathrm{Pt/rutile}}{0.5\%\ \mathrm{Ag/rutile}}$$

Such a behavior was confirmed by the comparison of the de-hydrogenation photoactivities of neat TiO_2-D (Degussa P-25), of Ag/TiO_2-D and of Pt/TiO_2-D, [23] with neat liquid 2-propanol (Fig. 2).

The curves of Fig. 2 can be interpreted as follows. Neat titania is able to produce some gaseous hydrogen but, after 1 to 2 h of UV-illumination, the active sites are exhausted and the reaction stops. When platinum is deposited, H_2 evolution is much stronger and truly catalytic with a constant reaction rate. When silver is deposited, the amount of hydrogen evolved is substantially higher than that of neat titania, but H_2 production levels off, as if some sites become progressively inhibited.

From kinetics and photoconductivity results [39], the reaction mechanism of alcohols can be described by eight consecutive elementary steps.

(1) Light absorption and electron-hole pair formation.

(2) Simultaneous dissociative alcohol chemisorption

$$CH_3\text{-}CHOH\text{-}CH_3 \rightarrow (CH_3)_2CHO^- + H^+ \qquad (15)$$

(3) Electron transfer of photoelectrons to silver and to platinum deposited on it (electron-hole separation):

$$e^-(TiO_2) + Pt_{(s)} \rightarrow e^-(Pt_{(s)}) \qquad (16)$$

(4) Neutralization of alcoholate ions by positive photo-holes into activated radicals (additional electron-hole separation).

(5) Deactivation of the alcoholic radical by loss of a hydrogen atom and formation of a ketone molecule which desorbs in the liquid phase:

$$CH_3\text{-}C^{\circ}OH\text{-}CH_3 \rightarrow CH_3\text{-}CO\text{-}CH_3(aq) + H^{\circ} \qquad (17)$$

(6) Migration on titania of H° atoms, probably as protons, towards negatively charged bimetallic particles via a reverse hydrogen spill over process.

(7) Neutralization of protons in a cathodic-like process at the surface of platinum with excess photoelectrons driven from TiO_2 to Ag–Pt particles:

$$H^+ + e^-(Pt_{(s)}) \rightarrow Pt_{(s)}\text{-}H \qquad (18)$$

where $Pt_{(s)}$ represents a surface platinum atom.

(8) Recombination of H atoms on $Pt_{(s)}$ into dihydrogen molecules which desorb into the gas phase through the liquid phase:

$$2Pt_{(s)}\text{-}H \rightarrow 2Pt_{(s)} + H_2(ag) \qquad (19)$$

This eight-elementary-step process is summarized in the cyclic scheme of Fig. 3. In long duration experiments, several hundreds of cycles have been performed on the same sites without any decline of photoactivity.

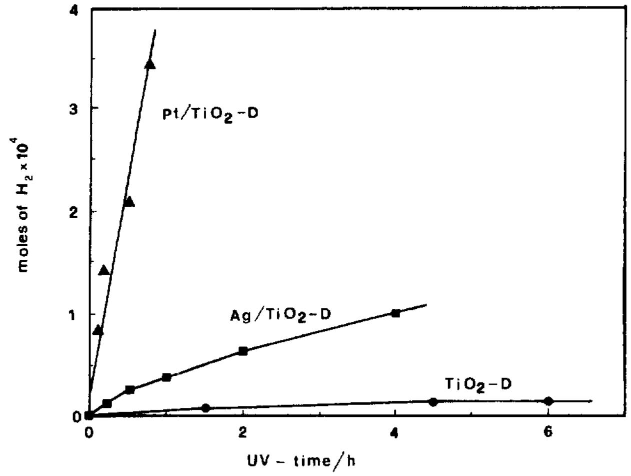

Fig. 2. Comparative kinetics of hydrogen evolution from pure 2-propanol ($n_{H_2}=f(t)$) for naked titania Degussa P-25 and for platinum and silver deposited catalysts.

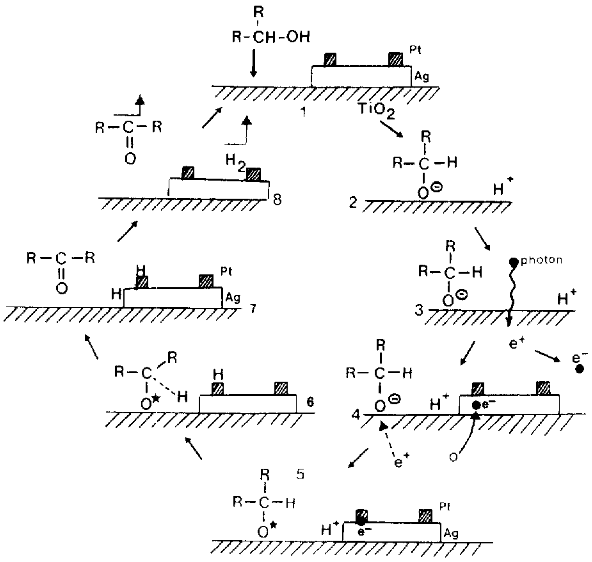

Fig. 3. Cyclic mechanism of the photocatalytic dehydrogenation of 2-propanol performed on Pt/Ag/TiO_2 catalysts at 300 K.

From the examination of the cyclic mechanism of Fig. 3, it can be seen that the photocatalytic process is bifunctional: the reaction initiates on the support (dissociative alcohol chemisorption, light absorption and electron-hole pair formation) but needs the contribution of the metal to make the system work catalytically (electron transfer, proton reduction and hydrogen recombination and evolution). The poor photoactivity of Ag/TiO_2 samples is not due to the absence of electron transfer to silver since this electron transfer has already been invoked in the preceding paragraphs for the photocatalytic oxidation of 2-propanol and especially for the photodeposition of platinum which selectively occurs on Ag particles (Section 1). It is rather due to the group IB transition metal nature of Ag, which is a very poor catalyst for hydrogen chemisorption and evolution.

The results of photocatalytic dehydrogenation confirm the STEM-EDX analysis of the photodeposition of platinum on Ag particles previously deposited. From Table 2, it can be seen that 0.5% Pt/anatase and 0.5% Pt/0.5% Ag/anatase have the same activities either in acetone or in hydrogen production. In addition, these values are equal to those found for 0.5% Pt/TiO_2-D (Table 2, last line) indicating that for the same platinum weight percentage, the concertation between platinum and anatase is equally efficient for 2-propanol dehydrogenation.

This means that platinum is deposited on silver particles with good electrical contacts between both metals. The photoelectrons are transferred from TiO_2 to silver and then from silver to platinum, on which photoreduction into hydrogen occurs. Silver only acts as an electrical relay without interfering with the reaction rate of hydrogen evolution.

In the dehydrogenation process, H_2 reduction appears to be under cathodic control. By contrast with what occurs for O_2 reduction, the presence of a metal catalyst increases the reduction rate of hydrogen over both anatase and rutile forms.

4. Concluding remarks

The influence of metallic silver deposits on the photocatalytic activities of both rutile and anatase allotropic forms of titania has been studied in three reactions which significantly differ according to the nature of reactant and of the reaction product phases: formation of a solid product (Pt photodeposition); reaction between a liquid and gas phase (2-propanol oxidation); reaction without gaseous reactant but with the formation of a gaseous product (2-propanol dehydrogenation). Whatever these differences, these three reactions have exhibited common features.

First, the deposit of silver on titania creates an electron transfer to the metal which persists whatever the nature of the ambient medium (vacuum, oxygen (or air), hydrogen, water). This electron transfer is catalytically beneficial in only two special cases: the localized photodeposition of Pt on Ag and the photo-oxidation of 2-propanol on rutile.

In the first case, silver deposits attract photoelectrons before transferring them to platinum (Pt^{IV}) complexes for an easier reduction to Pt°. In the second case, silver deposit on rutile favors the efficient electron-hole pair dissociation and/or reduces the electron-hole pair recombination.

In the case of anatase, the deposit of silver is detrimental when the electrons transferred to Ag cannot be favorably transmitted from the kinetic point of view, to another phase. In 2-propanol oxidation, electrons are accumulated in silver particles which subsequently attract holes and become recombination centers. By contrast, in the presence of platinum ions or complexes the transferred electrons are used for Pt^{IV} reduction. In the presence of deposited metallic platinum, the electrons are transferred from TiO_2 to Ag and then from Ag to Pt at the surface of which the electrons are used for proton reduction in 2-propanol dehydrogenation. The presence of a metal is beneficial when both reduction or oxidation are not under diffusion control, or near it. All three reactions are based on common electronic processes involving (i) the generation of photoelectrons on titania and (ii) the electron transfer to silver and to platinum.

Acknowledgements

The authors thank Mrs C. LECLERCQ for TEM and STEM analyses and M.N. Mozzanega for the essential experimental work performed. A.S. thanks the C.N.R. (Italy) for financial support N. 95.01197.CT03.

References

[1] M. Schiavello, M. (Eds.), Photocatalysis and Environment, Kluwer, Dordrecht, 1988.
[2] N. Serpone, E. Pelizzetti (Eds.), Photocatalysis, Fundamentals and Applications, Wiley, New York, 1989.
[3] D.F. Ollis, A. Al-Ekabi (Eds.), Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam, 1993.
[4] J.-M. Herrmann, H. Courbon, J. Disdier, M.N. Mozzanega, P. Pichat, in: G. Centi, F. Trifirò (Eds.) New Developments in Selective Oxidation, Stud. Surf. Sci. and Catal. Vol. 55, Elsevier, Amsterdam, 1990, p. 675.
[5] P. Pichat, Catalysis Today 19 (1994) 313.
[6] J.M. Herrmann, Catalysis Today 24 (1995) 157.
[7] K. Tanaka, N.F.V. Capule, T. Hisanaga, Chem. Phys. Lett. 187 (1991) 73.
[8] A.P. Rivera, K. Tanaka, T. Hisanaga, Appl. Catal. B: Environmental 3 (1993) 37.
[9] A. Sclafani, L. Palmisano, M. Schiavello, J. Phys. Chem. 94 (1990) 829.
[10] A. Sclafani, L. Palmisano, E. Davì, New J. Chem. 14 (1990) 265.
[11] K. Karakitsou, X.E. Verykios, J. Phys. Chem. 97 (1993) 1184.
[12] J.M. Herrmann, H. Courbon, P. Pichat, J. Catal. 72 (1981) 129.
[13] J.M. Herrmann, H. Courbon, P. Pichat, J. Catal. 95 (1985) 539.
[14] J.M. Herrmann, H. Courbon, P. Pichat, J. Catal. 108 (1987) 426.
[15] P. Pichat, J.M. Herrmann, J. Disdier, H. Courbon, M.N. Mozzanega, Nuovo J. Chim. 5 (1982) 627.
[16] C.M. Wang, A. Heller, H. Gerischer, J. Am. Chem. Soc. 114 (1992) 5230.
[17] H. Gerischer, A. Heller, J. Phys. Chem. 95 (1991) 5261.
[18] H. Gerischer, A. Heller, J. Electrochem. Soc. 139 (1992) 113.
[19] T. Kobayashi, H. Yoneyama, H. Tamura, J. Electrochem. Soc. 103 (1983) 1706.
[20] B. Kräutler, A.J. Bard, J. Am. Chem. Soc. 100 (1978) 5985.
[21] I. Izumi, F.F. Fan, A.J. Bard, J. Phys. Chem. 85 (1981) 218.
[22] I. Izumi, W.W. Dunn, K.O. Wilbourn, F.F. Fan, A.J. Bard, J. Phys. Chem. 84 (1980) 3207.
[23] A. Sclafani, M.N. Mozzanega, P. Pichat, J. Photochem. Photobiol. A: Chem. 59 (1991) 181.
[24] A. Wold, Chem. Mater. 5 (1993) 280.
[25] W. Mu, J.M. Herrmann, P. Pichat, Catal. Lett. 3 (1989) 7.
[26] G. Al-Sayyed, J.C. D'Oliveira, P. Pichat, J. Photochem. Photobiol. A: Chem. 58 (1991) 99.
[27] G. Irick, J. Appl. Polym. Sci. 16 (1972) 2387.
[28] T.A. Egerton, C.J.J. King, Oil Colour Chem. Ass. 62 (1979) 386.
[29] A. Sclafani, M.N. Mozzanega, J.M. Herrmann, J. Catal. 168 (1997) 117.

[30] J.M. Herrmann, J. Disdier, P. Pichat, J. Catal. 113 (1988) 72.
[31] J.M. Herrmann, J. Disdier, P. Pichat, J. Phys. Chem. 90 (1986) 6028.
[32] A. Fernandez, A. Caballero, A.R. Gonzalez-Elipe, J.M. Herrmann, H. Dexpert, F. Villain, J. Phys. Chem. 99 (1995) 3303.
[33] A. Henglein, J. Phys. Chem. 83 (1979) 2209.
[34] A. Henglein, J. Phys. Chem. 83 (1979) 2858.
[35] A. Henglein, Ber. Bunsenges. Phys. Chem. 84 (1980) 253.
[36] P.C. Lee, D. Meisel, J. Catal. 70 (1987) 160.
[37] J. Disdier, J.M. Herrmann, P. Pichat, J. Chem. Soc., Faraday Trans. I 79 (1983) 651.
[38] J.-M. Herrmann, J. Disdier, P. Pichat, in: B. Imelik et al., (Eds.), Metal-Support and Metal-Additive Effects in Catalysis, Stud. Surf. Sci. Catal., Vol. 11, Elsevier, Amsterdam, 1982, p. 27.
[39] J.-M. Herrmann, P. Pichat, in: G. Pajonk, S.J. Teichner, J.E. Germain (Eds.) Spillover of Adsorbed Species, Stud. Surf. Sci. Catal., Vol. 17, Elsevier, Amsterdam, 1983, p. 77.
[40] J.-M. Herrmann, in R.T.K. Baker, S.J. Tauster, J.A. Dumesic, (Eds.), Strong Metal-Support Interactions, A.C.S. Symp. Series, Vol. 298, 1986, p. 200.
[41] H. Tahiri, Thèse 3^e Cycle, Université d'Agadir, Morroco.
[42] G. Munuera, F.S. Stone, Discuss. Faraday Soc. 52 (1971) 205.
[43] R.J. Bickley, G. Munuera, F.S. Stone, J. Catal. 31 (1973) 398.
[44] J. Disdier, J.M. Herrmann, P. Pichat, J. Chem. Soc., Faraday Trans. I 77 (1981) 2815.
[45] H. Courbon, J.M. Herrmann, P. Pichat, J. Phys. Chem. 88 (1984) 5210.
[46] H. Courbon, P. Pichat, A. Sclafani, EuropaCat-I, Book of Abstracts Vol. 2, Montpellier 12–17 September, 1993, p. 727.
[47] K. Kobayatawa, Y. Nakazawa, M. Ikada, Y. Sato, A. Fujishima, Ber. Bunsenges. Phys. Chem. 94 (1990) 1439.
[48] R. Campostrini, G. Carturan, L. Palmisano, M. Schiavello, A. Sclafani, Mater. Chem. and Physics 38 (1994) 277.