NOTE

# Influence of Silver Deposits on the Photocatalytic Activity of Titania

The objectives of depositing metals over semiconductor photocatalysts are to improve the electron-hole pair separation and 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 studied belonged to group VIII. Very few studies concerned silver deposits (1). 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 last reaction (Pt/Ag/TiO$_2$) were also used as catalysts in two other test reactions to make 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 $\approx$ 1) (2), and (ii) its photocatalytic oxidation has been selected as a test reaction to evaluate the photocatalytic inertness of TiO$_2$-based pigments.

The solids used (50 mg) 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 nonporous particles). The photocatalytic mild oxidation and dehydrogenation of 2-propanol were performed in a batch photoreactor 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 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 equal to 50 mW cm^{-2}, which corresponds to a photonic flux of 4.18×10^{16} photons cm^{-2} s^{-1} directly absorbable by anatase.
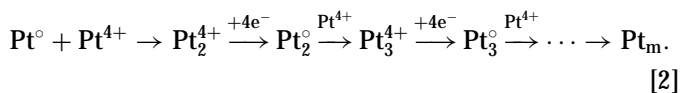
To prepare the Ag/TiO$_2$ samples (3), 500 mg of TiO$_2$ was suspended in 100 ml of an aqueous solution of AgNO$_3$ (Merck) of the desired concentration to get a final catalyst containing 0.5% Ag. The dispersion was deaerated with a rotatory pump for 15 min before UV illumination, which was maintained for 16 h to make sure that all silver was photodeposited. The suspension was then centrifuged. The solid was repeatedly washed with pure water and then dried in an oven at 353 K. The amounts of silver deposited were determined by chemical analysis of the solid.

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 photoreactor: the initial support was impregnated first in the dark in 10 cm^3 of a solution containing the total amount of platinum desired and prepared from a commercial solution of H$_2$PtCl$_6$, 6H$_2$O (Merck) containing 3.9 wt% Pt. A final weight percentage of 0.5% was chosen for both Ag and Pt. The photocatalytic deposition of platinum Pt^{IV} obeys the following stoichiometry (4):

$$Pt^{4+} + 2H_2O \xrightarrow{\text{TiO}_2 + h\nu} Pt^\circ + 4H^+ + O_{2(g)}. \qquad [1]$$
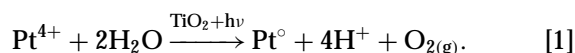
The agglomeration of Pt atoms into crystallites was proposed to occur via reduction as a cathodic-like process at small metallic nuclei

$$Pt^\circ + Pt^{4+} \rightarrow Pt_2^{4+} \xrightarrow[]{+4e^-} Pt_2^\circ \xrightarrow{Pt^{4+}} Pt_3^{4+} \xrightarrow[]{+4e^-} Pt_3^\circ \xrightarrow{Pt^{4+}} \cdots \rightarrow Pt_m. \qquad [2]$$

These solids were then examined by transmission electron microscopy (TEM) and by scanning transmission electron microscopy (STEM). After photodeposition of a low amount of silver (0.5 wt%), small Ag particles could be observed by TEM on the anatase sample. By contrast, on rutile, most of Ag was concentrated in very few large particles which are only present in some STEM micrographs. This indicates a very poor dispersion of silver on rutile.

After photodeposition of 0.5 wt% Pt on both types of titania already supporting Ag, some new particles of nanometric size were detected. By difference with the TEM micrographs, these particles could be ascribed to platinum crystallites. For anatase-based samples, 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. This indicated that platinum has been deposited as small crystallites on top of larger ones constituted by previously photodeposited silver. There is a 100% selectivity for platinum photodeposition on silver particles although chloroplatinic acid initially adsorbs on the whole anatase surface. This is due to an enrichment of

initially present Ag particles in photoelectrons (5, 6).

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

$$e^- + (Ag) \rightarrow e^-(Ag) \qquad [4]$$
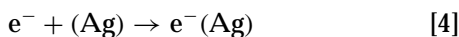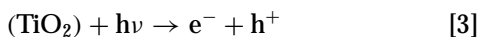
which converts Ag particles into small cathodes at the surface on which the photoreduction and the subsequent photodeposition of platinum readily occur,

$$4e^-(Ag) + (Pt^{IV}) \rightarrow Pt^\circ/Ag. \qquad [5]$$
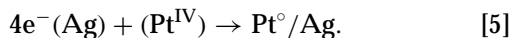
By contrast, on rutile, Pt deposits can be encountered either on top of silver or on rutile as small particles agglomerates. This difference in selectivity for local photodeposition of platinum can be explained by the poor dispersion of silver on rutile. TEM and STEM examinations of Ag/TiO₂ (rutile) have shown that most of silver deposit was concentrated in larger 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.

Acetone was the only organic product detected. The reaction rate did not change during at least the first 2 h. Therefore, the mean reaction rate based on 90 min of UV irradiation corresponded to the initial rate of reaction. Neat rutile is about three times less active than neat anatase. This ratio is comparable to the value found in Ref. (7). However, rutile and anatase have opposite behaviors in the presence of one or two metals: for rutile, metal deposits are beneficial, whereas for anatase they are in general detrimental. These results are in agreement with previous studies (8).

Rutile < 0.5% Ag/Rutile < 0.5% Pt/0.5% Ag/Rutile
< 0.5% Pt/Rutile

Anatase > 0.5% Pt/Anatase > 0.5% Ag/Anatase
> 0.5% Pt/0.5% Ag/Anatase

In the case of anatase, these results confirm the previous ones obtained on Pt/TiO₂ (Degussa P-25) in oxidation reactions, either in pure liquid organic phase (9) or in water solutions (8, 10). In the present reaction, a deposit of 0.5 wt% Pt on Degussa P-25 decreased the photocatalytic activity from 4.0×10^{-4} to 3.13×10^{-4} mol/h. This decrease is limited but, according to error limits, it is significant. The detrimental effect on the 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 the aqueous phase, the oxidation of 2-propanol involves OH° radicals generated by photoinduced holes h^+ (11, 12). 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 (13) performed *in vacuo*. The electron transfer was shown to persist under oxygen atmosphere (14). This means that less electrons are available for oxygen ionosorption at the surface of titania. 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. It can be easily conceived that if two metals are present, the electron transfer is more important and the inhibition of the reaction is 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 in agreement with Refs. (7, 8). This could be ascribed to less efficient adsorptive properties with respect to the oxygen (15–17) and/or to a higher rate of electron-hole recombination. Since both energy band gaps E_G are not very different (3.02 and 3.2 for rutile and anatase, respectively), it seems that the main reason for the lower activity of rutile cannot be explained only by its smaller light absorption capacity as suggested in Ref. (7).

The rates of photocatalytic dehydrogenation of 2-propanol

$$CH_3-CHOH-CH_3 \rightarrow CH_3-CO-CH_3 + H_2 \qquad [6]$$
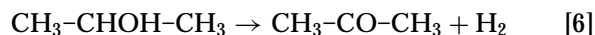
were calculated from the slopes of the straight lines of Fig. 1.

It is first confirmed that silver is a very poor (de)-hydrogenation metal cocatalyst, when compared to platinum. The same ratio of relative photoactivities (Pt/Ag) was obtained whatever the nature of titania:

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

Second, it is also confirmed that anatase is much more photoactive than rutile. The ratio of the number of moles 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
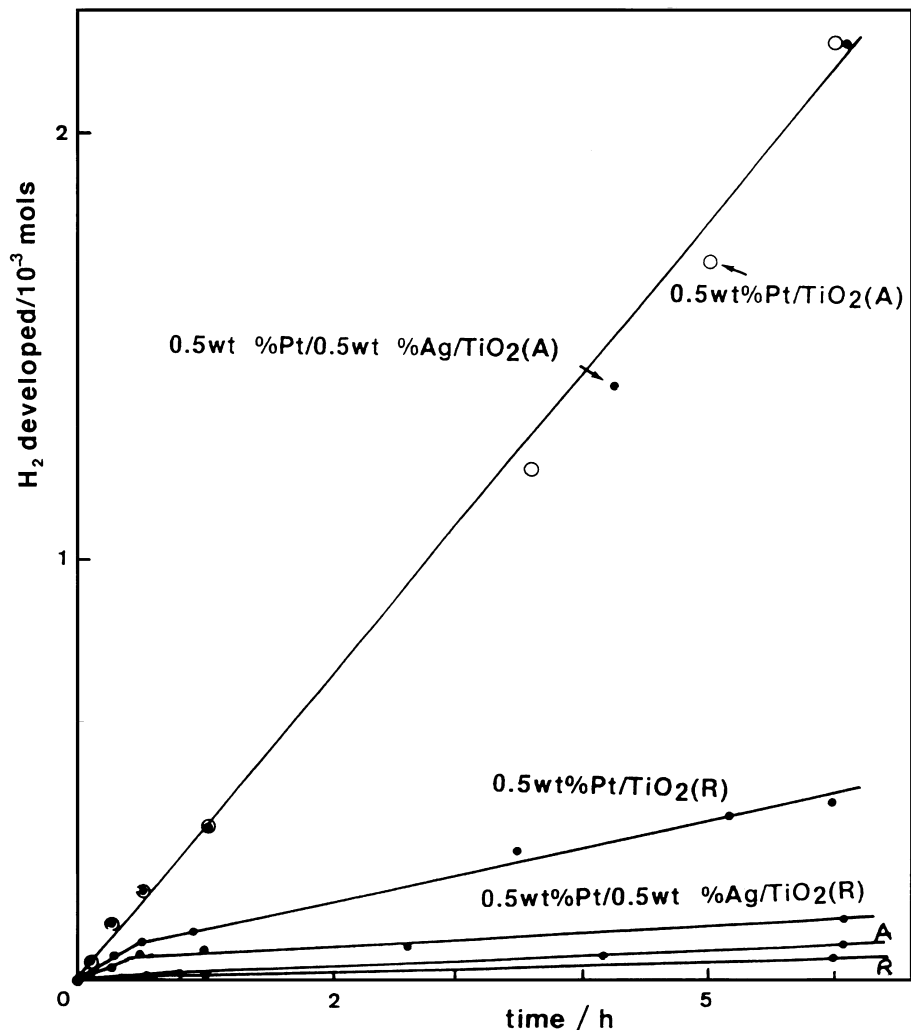
FIG. 1. Kinetics of hydrogen production in 2-propanol dehydrogenation performed in contact with Ag, Pt, and Pt–Ag metal catalysts deposited on anatase (A) and rutile (R). The two lower curves (A) and (R) refer to 0.5 wt% Ag deposited on anatase and rutile, respectively.

is equal to 4.2 and is identical to the ratio of that produced by 0.5 wt% Pt/anatase and 0.5 wt% Pt/rutile.

Pt/anatase (0.5%) and 0.5% Pt/0.5% Ag/anatase have the same activities either in acetone or in hydrogen production. These values are equal to those found for 0.5% Pt/TiO$_2$-D, indicating that for the same platinum weight percentage, the concertation between platinum and anatase cocatalysts is equally efficient for 2-propanol dehydrogenation. This is in agreement with STEM-EDX analyses which indicated 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 to hydrogen occurs.

In conclusion, the common feature for the three reactions was an electron transfer from illuminated TiO$_2$ to silver particles. The initial presence of silver orientates the localization of the subsequent Pt photodeposits with, in particular, a 100% selectivity to Pt deposition on top of silver particles or agglomerates previously deposited on anatase. In 2-propanol oxidation, Ag deposit was found beneficial for rutile and detrimental for anatase. For rutile, silver helps the electron-hole pair dissociation. For anatase, the negatively charged Ag particles preferentially attract photoholes and become recombination centers, thus decreasing the photocatalytic activity. For the dehydrogenation of 2-propanol, Ag/TiO$_2$ catalysts were found to be very poorly active, in line with the electronic structure of silver and its consequent poor reactivity with respect to hydrogen. However, in the simultaneous presence of platinum deposits, Pt/Ag/TiO$_2$ catalysts are as active as Pt/TiO$_2$ homologues, 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).

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