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Photocatalytic Dehydrogenation of Isopropanol on Pt/TiO_2 Catalysts

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Isopropanol which has been proposed as a "sacrificial" compound for the photodissociation of water in the presence of titania catalyst is photodehydrogenated into acetone on metal/TiO_2 catalysts. In the absence or in the presence of water vapor the amount of hydrogen produced is always equal to the amount of acetone. On the Pt/TiO_2 catalysts used the water-gas shift reaction is of a thermal nature and CO does not seem either to be a "sacrificial" compound. The mechanism of photodehydrogenation of isopropanol on Pt/TiO_2 catalysts is studied and the influence of the dispersion of Pt is discussed.

INTRODUCTION

It has been shown in previous work that in the presence of pure titania and oxygen the alcohols in the gas phase are oxidized partially into ketones and aldehydes under uv irradiation at room temperature (*1*, *2*). In the absence of oxygen in the stream of reactants, only a very limited oxidation reaction occurs with the surface lattice oxygen of TiO_2 with photodehydrogenation or similar processes being absent. In particular, in the flash irradiation of methanol and ethanol, on TiO_2 and ZnO, in the absence of oxygen, formaldehyde and acetaldehyde are formed (in a limited amount) through the interaction with the surface lattice oxygen and/or surface hydroxyls (*3*). These last species, converted to $OH^\cdot$ radicals by positive holes, were also assumed to be the initial agents of the photooxidation of isopropanol into acetone on TiO_2 (*4*), whereas the simultaneous formation of small quantities of formic acid and acetaldehyde was explained by dehydration of a fraction of the isopropanol and oxidation of the propene formed (*5*). Tertiary butanol gave acetone and isobutene in the same type of experiments (*6*) whereas isobutanol gave only isobutylaldehyde as would be expected from a primary alcohol (*7*).

Catalytic photosplitting of water on pure TiO_2 has been attempted but without success (*8*, *9*). The formation of nitrogen compounds (ammonia, hydrazine) from water and dinitrogen in the presence of irradiated TiO_2 containing divalent iron does not seem to be photocatalytic as it stops after reoxidation of iron (*10*). Attempts were made in this direction by associating TiO_2, with a second component in metallic (Pt, Rh) and/or ionic (RuO_2) form (*9*, *11–14*). The metal was, in particular, supposed to collect hydrogen species and release it as dihydrogen gas whereas the metal oxide was considered as being involved in the desorption of dioxygen. However, in almost all cases the formation of hydrogen from water is strongly limited because of the thermal back-reaction with oxygen on Pt (*9*), so a "sacrificial" system was proposed whereby a carbon-containing material (CO, hydrocarbons, alcohols, lignite, active carbon) functions as a scavenger of the generated oxygen (*11–13*, *15–17*). The question now arises whether for hydrogen-containing organic scavengers, like alcohols, dihydrogen is released by photosplitting of water or through the photodehydrogenation of the alcohol on TiO_2 containing Pt. If this second hypothesis is correct the photodecomposition of simultaneously present water may be a failure. In the presence of CO the water-gas shift reaction below 400 K

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was a sustained one and was explained by the photoenhanced redox mechanism of TiO_2 surface by CO and H_2O (*18*). It is not certain that the same mechanism will prevail for the couple H_2O–alcohol for energetic reasons (see below). Indeed, it has been found that for couples of linear C_1–C_4 primary aliphatic alcohols, as well as isopropanol, and liquid water the photoproduction of hydrogen was not correlated with the photosplitting of water but only with the photodehydrogenation of the alcohol (*19*) with the final production of an aldehyde (or ketone) but only a small amount of CO_2. The same conclusion has been formulated for the gas-phase photoreaction of the couple methanol–water.

EXPERIMENTAL

Reactor. A dynamic differential microreactor was used and has been described already in detail (*20*). The porous membrane supporting the powdered catalyst (20–40 mg) was cut from glass-fiber gauze (Wattmann GF/C) which is stable up to 200°C. The source of the uv radiation, filtered by a water screen from the ir, was a mercury-vapor 125-W lamp (Philips HPK 125). In a few cases the lamp SP 500 (500 W) was also used. A halogen 250-W lamp (Osram 24 V) was used, with a parabolic mirror, to increase the temperature of the catalyst (controlled by a thermocouple) above the ambient. The partial vapor pressure of reactants (isopropanol, water, acetone) in the carrier gas (nitrogen, 1 atm, with a flow of 30 cm^3 min^{-1}) was established through a saturation device at a controlled temperature. The analysis of effluents was performed by gas chromatography. High-purity reactants (gases and liquids) were used throughout.

Catalysts. The nonporous titania (anatase) support of 50 m^2 g^{-1} surface area was of a commercial origin (Degussa P25). For comparison purposes nonporous titania (anatase) aerosols, prepared by the flame reactor (*21*) and with surface areas of 17.7, 33, 70, and 140 m^2 g^{-1} were also used. The catalysts were prepared by impregnation with an aqueous solution of H_2PtCl_6 or $H_2Pt(OH)_6$ (10 cm^3 per g of TiO_2) of various concentrations depending on the desired Pt loading. The solvent was evaporated at room temperature in vacuum and the dry catalyst was pretreated at 400°C under various atmospheres in order to decompose the parent Pt salt. The following nomenclature gives the nature of the metal and of the support (metals other than Pt and supports other than TiO_2 were used for comparison purposes), the metal loading and the type of the pretreatment at 400°C (in N_2, O_2, or air and H_2). For instance, the catalyst (Pt–Ti–1.5) NH is 1.5% Pt on TiO_2 (50 m^2 g^{-1} unless otherwise stated) pretreated at 400°C during 16 h by nitrogen and then by hydrogen, whereas the catalyst (Pt–Ti–1) H contains 1% of Pt and is pretreated by hydrogen only. Nitrogen used for the pretreatment is of technical purity (<1% of O_2) and no difference was found for the characteristics and catalytic properties after pretreatment in air or O_2, instead of N_2 (see below). The chlorine content of the catalyst after any pretreatment at 400°C was reduced to less than 0.1%. It does not influence the catalytic properties, as is shown below by comparison with the catalyst prepared from $H_2Pt(OH)_6$. The dispersion of Pt was determined at 25°C by chemisorption of H_2 or titration O_2–H_2 (*22–24*), assuming in a conventional way the stoichiometry $Pt_{(s)}$–H where $Pt_{(s)}$ is a platinum surface atom (*25*).

RESULTS AND DISCUSSION

A. Characterization of Catalysts

Table 1 gives the dispersions of Pt for Pt/TiO_2 catalysts of various Pt loadings, pretreated at 400°C by N_2 and then by H_2.

The results in Table 1 show that both methods, chemisorption and titration, give very comparable results. The dispersion of Pt is of the order of 40 to 50% irrespective of metal loading and surface area of titania support, except for 7.6% Pt loading where

TABLE 1

Influence of Pt Loading on Pt Dispersion for Catalysts of the Series (Pt–Ti–x) NH (TiO_2: 50 m^2 g^{-1})

Catalyst	Dispersion (%)		Metallic surface area (m^2 g^{-1} Pt)		Diameter of Pt particles (Å)	
	A	B	A	B	A	B
(Pt–Ti–0.27)	—	44.0	—	121	—	23.0
(Pt–Ti–0.98)	44.3	52.6	122	151	23.0	18.5
(Pt–Ti–1.5)	22.0	36.8	60	102	46.7	27.4
(Pt–Ti–1.8)	46.5	54.4	128	123	21.8	22.7
(Pt–Ti–4.1)	41.2	43.7	124	131	22.6	27.5
(Pt–Ti–7.6)	12.4	16.6	24	46	81.8	61.2
(Pt–Ti–0.89)[a]	54.5	69.6	168	214	16.7	13.0
(Pt–Ti–1.0)[b]	—	54.4	—	167	—	16.7

Note. A, dispersion determined by chemisorption of H_2 at 25°C; B, dispersion determined by titration O_2–H_2 at 25°C.

[a] TiO_2 of 17.6 m^2 g^{-1} surface area.

[b] TiO_2 of 140 m^2 g^{-1} surface area.

the dispersion is lower or the diameter of the Pt particles higher. For all other catalysts this diameter is in the range of 20–30 Å. Transmission electron microscopy gives very similar results. The dispersion is not modified if the reduction by H_2 is carried out at 200°C instead of 400°C but is significantly decreased (by about 20%) for 500°C reduction.

Pt catalysts on a titania carrier were only recently introduced in connection with the SMSI effect and it is of interest to report the results for the direct reduction by H_2 at 400°C or after a pretreatment at 400°C by a nonreducing gas, other than N_2. These results are given in Table 2.

The results of Table 2 show that the direct reduction of the catalyst by H_2 (at 400 or at 200°C) is detrimental to the dispersion of Pt which does not exceed a few percentage points. Examination by TEM confirms the large diameter of Pt particles (in the range of a few hundreds Ångstroms). For all catalysts treated by a nonreducing gas at 400°C prior to the reduction the dispersion is much higher and does not depend on the nature of the gas. The dispersion is not modified if the reduced catalyst is handled in the ambient air and again reduced (samples NHH and HH). Finally, drying of the impregnated precursor under vacuum at 25°C (standard procedure) or in air at 110°C is also without any effect on the dispersion [samples (a) and (b)]. It is possible that the precursor (H_2PtCl_6 or $PtCl_4$) forms large agglomerates after drying (under vacuum at 25°C or in air at 110°C) which are then reduced by H_2 before the temperature of 400°C is attained in the direct reduction and thereby gives Pt particles of large dimensions. A thermal treatment at 400°C in O_2-containing atmosphere, prior to the reduction, probably leads to the formation of Pt oxychlorides which melt and migrate at high temperature on the TiO_2 surface, giving a more uniform layer which is finally reduced by H_2 treatment and results in high dispersion of Pt (*26*). If the initial thermal treatment is performed in a very pure N_2 (without O_2) the results of the dispersion are the same as those observed in a direct reduction by H_2, i.e., low dispersion. This behavior points out the beneficial influence of heating and probably melting of Pt oxy-

TABLE 2

Influence of the Nature of Pretreatment at 400°C on Pt Dispersion for Pt/TiO_2 (50 $m^2\ g^{-1}$) Catalysts

Catalyst	Dispersion (%)		Metallic surface area ($m^2\ g^{-1}$ Pt)		Diameter of Pt particles (Å)	
	A	B	A	B	A	B
(Pt-Ti-0.98)H	—	6.0	—	3	—	929
(Pt-Ti-4.1)H	2.1	2.8	6	11	479	359
(Pt-Ti-4.1)HH	1.3	4.7	4	13	767	215
(Pt-Ti-4.1)NH	41.2	43.7	124	131	22.6	21.5
(Pt-Ti-1.5)NHH	26.0	37.7	71	104	39.1	26.8
(Pt-Ti-1.5)NH	22.0	36.8	60	102	46.7	27.4
(Pt-Ti-1.5)OH	21.3	35.8	58	98	47.6	28.4
(Pt-Ti-1)CH	17.9	33.7	47	63	59.0	44.2
(Pt-Ti-1)OH[a]	—	40.2	—	121	—	23.2
(Pt-Ti-1)H[b]	9.8	5.3	9	15	308	195

Note. A and B: see Table 1. H, pretreatment at 400°C in H_2; NH, pretreatment at 400°C in N_2 and then in H_2; NHH, the catalyst NH in the ambient air, reduced again in H_2 at 400°C; HH, the catalyst H in the ambient air, reduced again in H_2 at 400°C; OH, pretreatment at 400°C in O_2 and then in H_2; CH, pretreatment at 400°C in air and then in H_2.

[a] Catalyst dried in air at 110°C (instead of vacuum at 25°C).

[b] Catalyst dried in air at 110°C and reduced in H_2 at 200°C.

chlorides (without reduction) and these then "wet" the support much better than chlorides. It is known that chlorides may be reduced in H_2 at fairly low temperatures giving the metal directly. With the precursor $H_2Pt(OH)_6$ on TiO_2 a very good dispersion (~50%) is obtained even for the series H catalysts (without N_2 pretreatment). This is not surprising since this precursor melts at 100°C and boils at 120°C.

It is also observed from the results of Tables 2 and 3 that the SMSI (strong metal–

TABLE 3

Catalytic Activity in Hydrogenation of Benzene at 50°C on (Pt–Ti–0.98) Catalysts of Series H and NH

Catalyst	Reduction temperature (°C)	Dispersion of Pt (%)		Reaction rate (mmol $C_6H_{12}\ g^{-1}$ catal. h^{-1})	Turnover frequency (molecule h^{-1})	
		A	B		A	B
(Pt–Ti–0.98)H	200	10	10	2.2	423	423
	400	—	6	0.2	—	33
	500	0	0	0	0	0
(Pt–Ti–0.98)NH	200	49.1	50.4	4.0	159	148
	400	44.3	52.6	4.0	176	147
	450	18.0	46.6	2.8	307	119
	500	28.8	43.0	1.1	77	52

Note. A and B: see Table 1.

support interaction) effect does not operate below 500°C on the dispersion measured by chemisorption of H_2 or titration by O_2–H_2. However, as is shown below, the dispersion of Pt plays only a secondary role for the photocatalytic dehydrogenation of isopropanol as the reaction starts on the TiO_2 surface. It is, on the contrary, of paramount importance in the thermal reaction of hydrogenation of benzene into cyclohexane at 50°C, as shown by the results of Table 3 concerning the catalysts of series H and NH.

It is interesting to observe that the SMSI effect after reduction of Pt at 500°C is more sensitive in hydrogenation of benzene for catalysts containing poorly dispersed Pt (series H). For Pt on other supports such as SiO_2 or Al_2O_3 it is recognized that hydrogenation of benzene is not structure sensitive and that the turnover frequency remains practically the same for any dispersion of the metal, which is not the case for the results of Table 3. Again, the pretreatment of Pt/TiO_2 catalysts at 400°C in a very pure N_2 (without O_2) gives practically the same results of dispersion and of catalytic activity in hydrogenation of benzene as for catalysts directly reduced in H_2 at 400°C (series H, Table 3) pointing out the influence of oxygen during the pretreatment of the precursor prior to the reduction.

B. Photoassisted Water Gas Shift Reaction

In an attempt to photodecompose water vapor on Pt/TiO_2 catalysts a flow of N_2 (30 cm^3 min^{-1}) saturated with H_2O at 25°C was directed into the photocatalytic reactor. No traces of H_2 or O_2 were recorded in the effluents, thus confirming the results of various authors mentioned previously. Experiments with CO as a scavenger of produced oxygen are equivalent to the photoassisted water-gas shift reaction. A mixture of reactants containing 11.8% of CO, 1.3% of H_2O, and 86.9% of He as a carrier gas (1 atm total pressure) was flowed into the photocatalytic reactor (30 cm^3 min^{-1}) containing the catalyst (Pt–Ti–4.1) NH. With the 125-W lamp (HPK 125) as a uv source no reaction products (CO_2 and H_2) were detected by gas chromatography. During this irradiation the temperature of the catalyst, measured by a thermocouple, is of the order of 30°C, at the most. Now, irradiation with the 500-W lamp (SP 500) immediately produces H_2 and CO_2. Curve 1 in Fig. 1 shows the rate of production of H_2 with time on stream. However, it appeared simultaneously that the catalyst temperature rose to about 140°C, despite all the precautions such as screening the lamp by water from the reactor. The reaction therefore seems to be thermal and not photocatalytic. This has already been observed on platinized $TiO_2(100)$ surface, above 400 K (127°C) (*18*). In an ordinary Pyrex dynamic differential microreactor (nonphotocatalytic) it has indeed been observed that on (Pt–Ti–4.1)NH catalyst the thermal reaction starts around 100°C and its rate increases with the temperature according to curves 2 and 3 of Fig. 1. The apparent activation energy in the range 120–220°C for this reaction is 92 kJ mol^{-1} and compares well with the value of 109 kJ mol^{-1} given in Ref. (*18*). The lack of success in using CO as the "sacrificial" compound, despite the favorable free energy change:

$$CO_{(g)} + H_2O_{(g)} \rightarrow CO_{2(g)} + H_{2(g)} \qquad \Delta G^\circ_{298} = -28.7 \text{ kJ mol}^{-1}$$

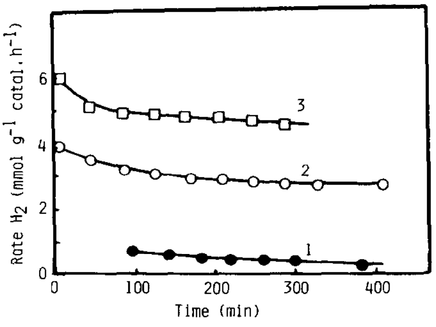

FIG. 1. Rate of formation of H_2 on Pt/TiO_2 catalyst in water-gas shift reaction. □, thermal reaction at 180°C; ○, thermal reaction at 164°C; ●, pseudophotocatalytic reaction.

may even lead to the use of isopropanol being rejected as "sacrificial" compound since with it the energy balance is unfavorable:

$$CH_3\text{–}CHOH\text{–}CH_{3(g)} + 5H_2O_{(g)} \rightarrow 3CO_{2(g)} + 9H_{2(g)} \qquad [1]$$

$$\Delta G^\circ_{298} = +133.5 \text{ kJ mol}^{-1}$$

The reaction in which oxygen released from water is used to oxidize isopropanol into acetone would be energetically neutral with respect to the dissociation of water (see below), unless the product of the oxidation of isopropanol is in a higher degree of oxidation than acetone. Now, acetone is very difficult to photooxidize (*1*) and even an aldehyde like propanal is not photooxidized by water (*19*).

C. Photodehydrogenation of Isopropanol

(*a*) *Reaction in the dark.* Isopropanol has already been used in the photosplitting of water (*12*). Preliminary experiments in our laboratory disclosed that the irradiation in the photocatalytic reactor by the lamp HPK 125 of a mixture of water and isopropanol vapors in nitrogen as a carrier gas in the presence of Pt/TiO_2 catalyst gives hydrogen and acetone. However, it has also been observed that similar results are obtained with isopropanol alone, without water. These results may therefore be understood as a simple photodehydrogenation of isopropanol and not a photosplitting of water in the presence of the "sacrificial" compound. A detailed study of this reaction was carried out in the following conditions: partial pressure of isopropanol = 17 Torr, temperature = 30°C, mass of the catalyst = 10–15 mg, overall gas flow at 1 atm = 30 $cm^3 \, min^{-1}$. The conversion in the differential photoreactor conditions was of the order of 2%. The energy balance:

$$CH_3\text{–}CHOH\text{–}CH_{3(g)} \rightarrow CH_3\text{–}CO\text{–}CH_{3(g)} + H_{2(g)}$$

$$\Delta G^\circ_{298} = 20.5 \text{ kJ mol}^{-1}$$

is favorable for the conversion of 10.6% of isopropanol under 17 Torr partial pressure. Preliminary experiments showed also that in the absence of uv irradiation the reaction starts around 70°C on the catalyst (Pt–Ti–1.8) NH and that the activation energy is 72.4 kJ mol^{-1}. The reaction products are propene, hydrogen, and acetone (with the selectivity in dehydrogenation higher than 95%). The same thermal reaction with practically the same selectivity in dehydrogenation is observed at 70°C on Pt deposited on other supports such as alumina or active carbon. On pure TiO_2 (50 $m^2 \, g^{-1}$) the reaction requires at least 220°C to proceed with a comparable rate but the selectivity in dehydrogenation is only 25%, the formation of propene being the main reaction (75%), and the activation energy is 138 kJ mol^{-1}. These results show that the thermal reaction of dehydrogenation at moderate temperatures (above 70°C) is due to Pt, irrespective of the nature of the carrier, whereas pure TiO_2 (without Pt) is not active in a sustained thermal reaction below 220°C.

(*b*) *Reaction under irradiation.* In the absence of uv light no reaction is observed at 30°C. The analyses of effluents, made 5 min after the start of irradiation with lamp HPK 125, lead to curves of Fig. 2 showing the rate of formation of hydrogen and acetone. Only during the first few minutes did the amount of acetone exceed slightly that of hydrogen. This behavior is probably due to

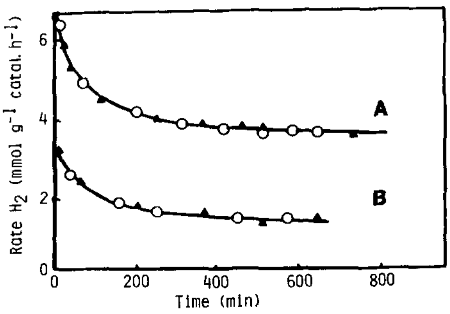

FIG. 2. Rate of formation of acetone or of hydrogen on Pt/TiO_2 catalysts under uv irradiation (p_{iso} = 17 Torr). (A) (Pt–Ti–0.98) NH catalyst, (B) (Pt–Ti–0.98) H catalyst; ▲, acetone, ○, hydrogen.

the photoreaction of isopropanol with surface lattice oxygen of TiO_2 and eventually to traces of air in the reactant inlets. The catalyst of the series NH is more active (Fig. 2) than the catalyst of the series H. This problem is examined below with respect to the dispersion of Pt. This dispersion has no influence on the achievement of the steady state in Fig. 2 which is observed after about 5 h on stream. This time lag may be reduced by introducing water vapor (a few Torr) in the feed (see below). Alcohol photoreduces the surface of TiO_2 (*1, 3–6*) whereas in the presence of H_2O this reduction is counterbalanced (*27*) and a steady state with a less-reduced surface is more rapidly established. Moreover, water influences one of the steps of the reaction as is discussed below.

The activation energy of the photodehydrogenation of isopropanol is 9.2 kJ mol^{-1}. Various tests were made in the same experimental conditions in order to show that this reaction requires a simultaneous presence of a metal (Pt) and of a photoactive support (TiO_2). For instance, catalysts with Pt supported on SiO_2 or Al_2O_3 were inactive. On the other hand pure TiO_2 (50 m^2 g^{-1}) produces, only at the beginning of the test, a very limited amount of acetone and water vapor. It simultaneously turns blue which shows that isopropanol is oxidized to acetone by surface lattice oxygen of titania (*28*). The presence of hydrogen is not recorded. The photocatalytic dehydrogenation of isopropanol therefore requires the association of a metal (Pt) with a photoactive carrier (TiO_2).

The reaction is not controlled by intergranular diffusion because for a mass of catalyst [(Pt–Ti–0.98) NH] of 15 mg and for a given partial pressure of isopropanol (17 Torr) the partial pressure of hydrogen or acetone produced is directly proportional to the contact time or to the reciprocal of the overall flow rate (from 15 to 60 cm^3 min^{-1}). For a given overall flow rate (30 cm^3 min^{-1}) the partial pressure of hydrogen or acetone produced increases linearly with the mass of the catalyst, uniformly spread on the porous membrane in the reactor, up to a critical mass m_0. This behavior was already observed and explained (*29, 30*) by the critical thickness of the catalytic bed which limits the availability of the uv light to the bottom layers of the catalyst.

Pt is not the only metal which on TiO_2 gives an active catalyst. The influence of the nature of the metal deposited by impregnation on titania (50 m^2 g^{-1}) is shown in Table 4 giving the rates of formation of products at the steady state.

In the absence of dispersion measurements (Pt excepted) for comparable loadings of metals only qualitative comparison is made. It is however known that with the exception of Ni, which is less dispersed (*31*), the dispersions obtained with noble metals (Pd, Ru) are comparable to that of Pt. Assuming that Ni is poorly dispersed it appears that Pt is only four times more active than the less-active metal (Ni). This ratio (4 : 1) is much smaller than the ratio of rates of the thermal hydrogenation of benzene on the same catalysts (*32*). For instance, the Pt/TiO_2 catalyst of Table 4 exhibits an activity of 400 mmol of C_6H_{12} (g Pt)$^{-1}$ h^{-1}, whereas Ni/TiO_2 catalyst shows a negligible activity. This behavior shows that unlike for the thermal reaction the nature of the metal deposited on TiO_2 is less

TABLE 4

Photocatalytic Activity in the Dehydrogenation of Isopropanol at 30°C on Various Metals Deposited on TiO_2 and Reduced at 400°C

Metal	Loading (%)	Rates of formation (mmol g^{-1} catal. h^{-1})		Activation energy (kJ mol^{-1})
		H_2	Acetone	
Pt	0.98	3.7	3.8	9.2
Pd	0.5	2.4	2.4	15.9
Ru	0.9	1.4	1.3	—
Ni	0.7	0.9	1.0	14.6
Cu	1.0	0.0	0.0	—

critical (Table 4) for the photocatalytic reaction; this points out the secondary role of the metal which, in this reaction, only collects and releases hydrogen to the gas phase (*9*, *11–14*). Also for the metals of Table 4 the activation energy values are small and of the same magnitude (8–16 kJ mol^{-1}) which is a common feature for photocatalytic reactions which are not thermally activated (*1*, *18*). It has been mentioned previously that the activation energy in the thermal dehydrogenation of isopropanol on Pt/TiO_2 catalyst is 72.4 kJ mol^{-1}. Cu is inactive (Table 4) in the photodehydrogenation whereas this metal is active in the thermal dehydrogenation of a secondary alcohol (sec-butanol) (*33*) but at higher temperatures. It is well known that Cu does not significantly adsorb hydrogen at room temperature and therefore its role as a collector of photoproduced hydrogen species may be very much restricted.

(*c*) *Influence of Pt content of catalysts.* The role of the metal in a photocatalytic reaction occurring on the surface of TiO_2 may be clarified by the study of the influence of metal loading. For various thermal reactions the catalytic activity is proportional to the metal surface area (structure insensitive reactions) and the turnover frequency remains constant, irrespective of the dispersion of the metal provided that the SMSI effect is not operating. Pt on supports other than TiO_2 is not active in the photodehydrogenation of isopropanol (see above). If Pt is a collector of hydrogen species photoproduced on TiO_2 the surface density of Pt on TiO_2 may have an influence on the rate of release of H_2, because these species have to migrate on the TiO_2 surface for some distance before they meet a Pt site. The rate of the reaction at 30°C at the steady state (pressure of isopropanol: 17 torr) for catalysts of series H and NH is given in Table 5. This rate (formation of H_2 in mmol h^{-1}) is expressed either per gram of Pt or per gram of catalyst.

The results for well-dispersed Pt (NH series) are shown in Fig. 3 (curve a, per gram of catalyst, curve b, per gram of Pt). The representation of catalytic activity per gram of Pt necessarily implies that the metal is the site of the catalytic reaction. Curve b of Fig. 3 would then give an impression that the reaction is structure sensitive (in a wrong direction) because for almost the same dispersion of Pt in these catalysts (Table 5) the activity decreases when Pt loading or Pt surface area increases, whereas the metallic surface per g of Pt practically does not change (Table 1). The trend of curve b in Fig. 3 would then mean a decreasing turnover frequency when the loading increases. All catalysts were reduced at 400°C, a temperature at which the SMSI effect is not yet operative, as shown before. Now, it has been pointed out that Pt on TiO_2 without uv irradiation, is not a catalyst

TABLE 5

Photocatalytic Activity of Pt/TiO_2 Catalysts of Various Pt Loadings for Series H and NH

Catalysts (Pt–Ti–*x*)H		Rate (mmol H_2 h^{-1})		Catalysts (Pt–Ti–*x*)NH		Rate (mmol H_2 h^{-1})	
Pt% (*x*)	Dispersion (%)	(g^{-1} Pt)	(g^{-1} catal.)	Pt% (*x*)	Dispersion (%)	(g^{-1} Pt)	(g^{-1} catal.)
—	—	—	—	0.01	—	7450	0.74
—	—	—	—	0.05	72.0	2000	1.0
—	—	—	—	0.27	44.0	780	2.1
0.98	6	155	1.5	0.98	52.6	380	3.7
1.5	2	260	3.9	1.5	36.8	280	4.1
4.1	2.1	98	4.0	4.1	47.7	100	4.1
7.6	—	50	3.8	7.6	16.6	51	3.8

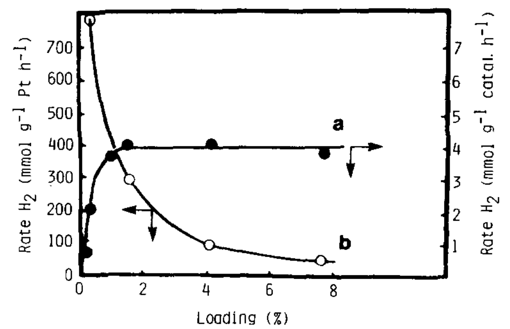

FIG. 3. Influence of Pt loading on TiO_2 (50 m^2 g^{-1}) support on the photocatalytic activity at the steady state. Catalysts of the series NH. (a) Rate of formation of hydrogen (or acetone) calculated per gram of catalyst. (b) Calculated per gram of Pt.

for the dehydrogenation of isopropanol at room temperature. The irradiated surface of TiO_2 must play a decisive role. If hydrogen from the alcohol is collected by Pt as H_2 and released to the gas phase, without being oxidized to water by TiO_2 lattice surface oxygen (limited reaction) or by oxygen from the gas phase (*1*, *2*, *29*), the reaction is sustained. If the surface of TiO_2 is involved in the photocatalytic activity, the rate of the reaction would be correlated with the extent of this surface. Curve a of Fig. 3 shows the activity per gram of catalyst. The surface of the support (TiO_2: 50 m^2 g^{-1}) screened by Pt is at the most 3.5 m^2 g^{-1} (for a Pt loading of 7.6%). Curve a therefore represents practically the activity of the same surface of the support. This activity increases with Pt loading up to a limit only (for Pt loadings lower than 1%) and then remains independent (horizontal portion of curve a). For Pt loadings below 1% when the dispersion of the metal is practically the same but the density of Pt sites per unit surface of TiO_2 decreases, the photoactivity decreases (to zero for pure TiO_2). This decrease below a ceiling value (horizontal portion of curve a) may be associated with some rate-determining step, depending on the density of Pt sites, dispersed on the TiO_2 surface when the density ceiling value is not yet attained (for low loadings). When it is attained (horizontal portion of curve a) this rate-determining step no longer operates and the reaction becomes controlled by a different step, independent of the surface density of Pt sites. The same trend is observed for catalysts of series H with the ceiling value of Pt loading increased to 1.5%.

The behavior just described was explained by the reverse spillover of hydrogen species, from the titania surface to Pt sites where it is released as H_2 (*34*). For a density of Pt sites below the ceiling value this migration of hydrogen species is rate determining.

(*d*) *Influence of the surface area of* TiO_2. Catalysts with 1% Pt loading on nonporous titania aerosols with various surface areas were prepared by impregnation with H_2PtCl_6. They belong to the NH series and the dispersion of Pt is almost the same (around 50%) for all samples. Their photoactivity at the steady state in the photodehydrogenation of isopropanol is given in Table 6.

For an eightfold increase of the surface area of the support a twofold increase of the rate (per gram of catalyst) is observed. The photohole transport to the surface of the TiO_2 particles of Table 6 is not affected by the TiO_2 particle size (ranging from 100 Å for 140 m^2 g^{-1} sample to 850 Å for 17.6 m^2 g^{-1} sample). Indeed, the depth of penetration of uv light of band-gap energy into TiO_2 is of the order of 330 Å, whereas the diffusion length of holes is 1.2 μm (*35*). Also for all particles of the catalyst penetrated by

TABLE 6

Photodehydrogenation of Isopropanol on 1% Pt/TiO_2 Catalysts with Various TiO_2 Supports

S_{BET} of TiO_2 (m^2 g^{-1})	Pt loading (%)	Dispersion (%)	Rate (mmol H_2 h^{-1})	
			(g^{-1} catal.)	(m^{-2} catal.)
17.6	0.9	54	1.9	0.107
33	1.0	—	2.1	0.063
50	1.0	52	3.7	0.074
70	1.0	—	2.8	0.040
140	1.0	57	4.0	0.029

the uv light all photogenerated holes can diffuse onto the surface and participate in the reaction. Now, in all cases the total amount of the sample was exposed to uv as the mass (or the thickness of the layer) of the catalyst, uniformly spread on the porous membrane, and always smaller than that the critical mass m_0 (*29, 30*). If the surface concentration of holes is proportional to the uv absorption area and as the total area of the sample seems to be irradiated, the rate per square meter of sample should be constant if only TiO_2 is the site for the photoreaction. This is not the case for the results of Table 6, which show that the rate per square meter decreases when the surface area of TiO_2 increases. Now, for almost the same dispersion of Pt the surface density of Pt sites decreases when the surface of the support increases. If the ceiling density of Pt sites is not obtained on these catalysts (it is already not obtained for titania of 50 m^2 g^{-1}, Fig. 3a) the reverse spillover of hydrogen species has to occur on still higher distances for higher surface area supports and the activity per square meter of catalyst (or practically of the support) decreases when this surface area increases.

(*e*) *Influence of the nature of the precursor and of the pretreatment.* Pt-on-titania catalysts are not very common and they have been mainly studied with respect to the SMSI effect. However, for photocatalytic reactions titania is one of the very few supports which, because of its photoactivity, cannot be substituted for photoinactive materials such as silica or alumina. Also the description of the photocatalytic behavior of these catalysts when the conditions of their preparation are varied may be of interest as it has not yet been studied from this point of view.

TABLE 7

Photodehydrogenation of Isopropanol on Pt/TiO_2 Catalysts Obtained from H_2PtCl_6 or $H_2Pt(OH)_6$

Precursor	Catalyst	Rate (mmol H_2 g^{-1} catal. h^{-1})
H_2PtCl_6	(Pt–Ti–1)nr[a]	1.7
	(Pt–Ti–0.98)NH	3.7
$H_2Pt(OH)_6$	(Pt–Ti–1)nr[a]	4.0
	(Pt–Ti–1)NH	4.1

[a] nr = catalyst impregnated, dried at room temperature, and nonreduced.

TABLE 8

Influence on the Photocatalytic Activity at the Steady State of the Temperature of Pretreatment in O_2 for the Catalyst (Pt–Ti–0.98)OH Reduced in H_2 at 400°C (TiO_2 = 50 m^2 g^{-1})

Temperature of pretreatment (°C)	Rate of formation (mmol g^{-1} catal. h^{-1})	
	Hydrogen	Acetone
[a]	1.6	1.6
110	2.3	2.3
225	3.9	3.9
325	3.8	3.7
400	3.9	3.9
600	3.1	3.1
700	3.1	3.1

[a] Catalyst (Pt–Ti–0.98)H, directly reduced in H_2 at 400°C.

The nature of the precursor, H_2PtCl_6 or $H_2Pt(OH)_6$, is not of paramount importance in the photocatalytic activity, as shown by the results of Table 7.

For NH series catalysts the activity (at the steady state) is comparable for both precursors as is comparable the dispersion of Pt (~50%). A difference is observed for nonpretreated and nonreduced catalysts (nr series). The reduction at room temperature by the reactants seems to be more difficult for the H_2PtCl_6 precursor, whereas for the $H_2Pt(OH)_6$ precursor the activity and the dispersion of Pt are very comparable to those of this catalyst in the NH series. The reasons for this behavior have been discussed previously. It is also of interest to report the catalytic behavior of catalysts (H_2PtCl_6 precursor) after various temperatures of pretreatment in N_2 (containing <1% of O_2) or O_2 (both atmospheres have the same influence on the properties, see

Table 2) before the reduction in H_2 at 400°C (Table 8), or after various temperatures of reduction.

The photocatalytic activity is constant for a pretreatment temperature between 200 and 400°C as so is the dispersion of Pt (~50%) and the surface area of the catalyst. It decreases only (by 20%) for pretreatment temperatures above 400°C (where the surface area of TiO_2 also decreases by 20%). Entirely parallel results are obtained for a fixed pretreatment temperature (400°C) but for reduction temperatures varying from 200 to 500°C. This behavior in the photocatalytic reaction of thermally pretreated catalysts (series NH or OH) is therefore very similar to their behavior in the hydrogenation of benzene (Table 3). This similarity between photocatalytic and catalytic reactions is still more evident from the kinetic study of the photocatalytic reaction which seems to follow a Langmuir-type mechanism.

D. Kinetic Studies

The apparent activation energy for the photocatalytic dehydrogenation of isopropanol (at the steady state) is 9.2 kJ mol^{-1} below 60°C. These values are of the same order as those found for photocatalytic oxidation of paraffins on pure TiO_2 in the same temperature range (*1*). Above 65°C the *thermal* reaction of dehydrogenation of isopropanol starts, with an activation energy of 72.4 kJ mol^{-1}.

The influence of the partial pressure of isopropanol (p_{iso}), in the range 3–17 Torr, was studied at 30°C for 1% Pt deposited on titania samples of surface areas from 33 to 140 $m^2\ g^{-1}$ (NH series, Table 6). In all cases the rate of formation of hydrogen or acetone follows the Langmuir-isotherm-based rate equation

$$\text{Rate} = k\frac{K_{iso}p_{iso}}{1 + K_{iso}p_{iso}}.$$

An increase of the partial pressure of acetone (p_{ac}), in the range 0.3–30 Torr, for a constant partial pressure of isopropanol (17 Torr), produces a decrease of the rate of the photoreaction according to the Langmuir model of competitive adsorption:

$$\text{Rate} = k\frac{K_{iso}p_{iso}}{1 + K_{iso}p_{iso} + K_{ac}p_{ac}}.$$

This model is compatible with the dehydrogenation of the adsorbed alcohol as a rate-determining step (*33*). Hydrogen pressure up to 320 Torr is without any effect on the rate of formation of acetone (with p_{iso} = 17 Torr). This absence of the forward spillover inhibiting effect, already discussed (*34*) can be understood if it is recalled that in the photocatalytic reaction under investigation photoactive sites (TiO_2) and metallic sites are simultaneously required. In a thermal dehydrogenation reaction on a metal the increase of hydrogen pressure would create conditions for the reverse reaction as no interconversion of species, adsorbed and reacting, is required for one type of site (metal). In the present case, if hydrogen species generated from adsorbed alcohol, which is transformed into a surface –OR group (*36, 37*), is in the form of H^+ (*38*) either as a result of the heterolytic dissociation of the alcohol or by the trapping of positive holes, it has to migrate to Pt enriched in electrons under uv irradiation (*39*) in order to be released as dihydrogen. These photoexcited electrons collected by Pt may create a potential barrier for gaseous H_2 for its adsorption, dissociation, and loss of electrons (to become H^+).

E. Influence of Water Vapor on the Photocatalytic Activity

If alcohol is a "sacrificial" compound for the photosplitting of water, more hydrogen would be released than by a mere photodehydrogenation of alcohol. The reaction in which the oxygen released from water is used to oxidize isopropanol into acetone would be energetically neutral with respect to the dissociation of water because of the equations

$$H_2O \rightarrow H_2 + \tfrac{1}{2}O_2$$

$$CH_3\text{-}CHOH\text{-}CH_3 + \tfrac{1}{2}O_2 \rightarrow CH_3\text{-}CO\text{-}CH_3 + H_2O$$

or by summing up:

$$CH_3\text{-}CHOH\text{-}CH_3 + H_2O \rightarrow CH_3\text{-}CO\text{-}CH_3 + H_2 + H_2O$$

and moreover it has been shown here that isopropanol may be directly photodehydrogenated to hydrogen and acetone:

$$CH_3\text{-}CHOH\text{-}CH_3 \rightarrow CH_3\text{-}CO\text{-}CH_3 + H_2.$$

Hence water is not needed to release hydrogen from isopropanol. Now, in all experiments with the mixture of the vapors of isopropanol and water the ratio of the rates of formation of hydrogen and of acetone was always found to be extremely close to one. Therefore no hydrogen excess was released in these conditions and also CO_2 was not detected, as would imply a "sacrificial" behavior of isopropanol (Eq. [1]). The rate of the photocatalytic reaction at the steady state is however accelerated by the presence of water vapor if its pressure does not exceed 10 Torr (for p_{iso} = 10 Torr). This effect is perfectly reversible as shown in Fig. 4. The suppression of water in the feed lowers the photocatalytic activity to the previous level and reciprocally. For higher pressures of water vapor (Table 9) the steady-state activity drops but remains still higher than for the dry alcohol.

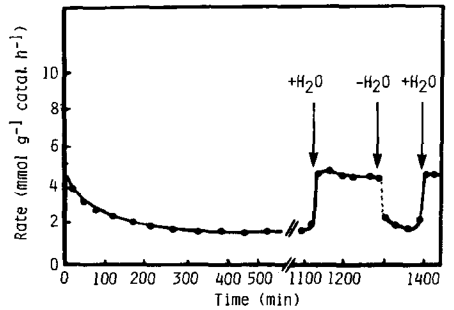

FIG. 4. Influence on the rate of formation of H_2 of the introduction of water vapor (6.8 Torr). Catalyst (Pt–Ti–0.98) NH (p_{iso} = 10 Torr).

TABLE 9

Influence of Water Vapor Pressure on the Photocatalytic Activity of the Catalyst (Pt–Ti–0.98)NH (p_{iso} = 10 Torr)

H_2O pressure (Torr)	Rate (mmol H_2 or acetone g^{-1} catal. h^{-1})
0	2.3
6.1	3.9
8.3	4.7
10.0	5.0
15.8	3.4

The decrease of the activity for water pressure exceeding 10 Torr may be explained by a competitive adsorption of both compounds on TiO_2 which finally cancels the initial favorable influence of water. It has been found, indeed, that water and isopropanol compete for the same adsorption sites (*4*,*5*) during the photooxidation of isopropanol on rutile. Water molecularly adsorbed on rutile surface has been arbitrarily divided into a "weakly" adsorbed fraction (removable by evacuation) and a "strongly" adsorbed fraction (*39*). Figure 4 shows that in the present case (all samples contain more than 92% of anatase) water may be considered as weakly adsorbed. Assuming that the behavior of anatase toward the adsorption of isopropanol, acetone, and water is very similar to the behavior of rutile, the results obtained on rutile (*39*) may cast some light on the influence of water vapor (Fig. 4) during the photodehydrogenation of isopropanol. Water weakly adsorbed from the gas phase does not displace preadsorbed isopropanol on rutile. The same effect must also be encountered in the case of anatase, because otherwise the rate of reaction would decrease, and this is exactly opposite to the phenomenon registered in Fig. 4. Now water from the gas phase displaces preadsorbed acetone (up to 10% of the adsorbed layer) but not isopropanol (*39*). This effect could explain the enhancement of the rate of the photodehydrogenation (Fig. 4), as isopropanol and acetone compete for the same sites. However, this type of behavior is only observed on catalysts of series NH whose Pt content does not exceed 1%. For catalysts of higher Pt content, i.e., catalysts on the horizontal line of Fig. 3a, no beneficial influence of water vapor pressure on the rate is recorded. This behavior was explained (*34*) by the rate, increased by H_2O, of the reverse hydrogen spillover (probably as H^+) provided that the density of Pt sites (below 1.5% Pt loading) makes this reverse spillover rate determining.

CONCLUSIONS

The photodehydrogenation of isopropanol in the gas phase at room temperature under uv irradiation is possible on titania provided that a dispersed metal, such as Pt, is simultaneously present. Its role consists in collecting the photoproduced hydrogen, whereas the alcohol is converted into acetone. The reaction does not occur at room temperature in the dark on Pt/TiO_2, or under uv on a metal supported on SiO_2, Al_2O_3, or carbon instead of TiO_2. Attempts to photosplit water vapor in the presence of isopropanol (or CO) were unsuccessful and show that isopropanol is not a "sacrificial" compound in this reaction, in disagreement with what has been claimed in some previous work. The rate of the photocatalytic dehydrogenation of isopropanol may be increased by the presence of water vapor; however, the amounts of hydrogen and acetone produced are in a ratio which remains extremely close to one, similarly as without water vapor. This increase of the rate is explained by a favorable influence of water vapor in the migration toward Pt sites of hydrogen species, photoreleased from alcohol on TiO_2 sites. This effect, however, is only recorded for Pt loadings (of the same dispersion) not exceeding a ceiling value, or a ceiling density of Pt sites on the surface of TiO_2. This reverse spillover is no longer rate determining for a higher density of Pt sites than the previous ceiling value. For all catalysts, however, the global rate-determining step is the photodehydrogenation of isopropanol in the adsorbed phase according to a Langmuir model, assuming simultaneously a competitive adsorption of photoproduced acetone. The mechanism of the photodehydrogenation should also include photonic steps (*1*) which may be summarized as

(a) Adsorption of isopropanol on TiO_2 and eventually its dissociation (homolytic):

$$(CH_3)_2CHOH_{(g)} + TiO_{2(s)} \rightleftarrows (CH_3)_2CHOH_{(ads\ TiO_2)}$$

or

$$(CH_3)_2CHO^{\cdot}_{(ads\ TiO_2)} + H^{\cdot}_{(ads\ TiO_2)}$$

(b) Under uv irradiation of TiO_2 with photons of energy higher than the band gap of the solid (3.1 eV, or wavelength 400 nm) an electron-hole pair is created. Platinum traps electrons (*40*), whereas positive holes may be trapped by adsorbed isopropanol which then release a proton H^+:

$$TiO_2 + h\nu \rightleftarrows h^+ + e^-_{(Pt)}$$

$$(CH_3)_2CHOH_{(ads\ TiO_2)} + h^+ \rightarrow (CH_3)_2CHO^{\cdot}_{(ads\ TiO_2)} + H^+_{(ads\ TiO_2)} \quad [1]$$

The protons are collected by Pt enriched in electrons:

$$H^+_{(ads\ TiO_2)} + Pt^- \rightarrow TiO_2 + Pt{-}H \quad [2]$$

$$Pt{-}H \leftrightarrows Pt + \tfrac{1}{2}H_{2(g)}$$

A second proton is similarly released from the adsorbed alcoxy species:

$$(CH_3)_2CHO^{\cdot}_{(ads\ TiO_2)} + h^+ \rightarrow (CH_3)_2CO_{(ads\ TiO_2)} + H^+_{(ads\ TiO_2)} \quad [3]$$

This scheme accounts for a quantum yield of 0.5. In the photodehydrogenation of alcohols on TiO_2 in the liquid phase the quantum yield observed was 0.45 for methanol and much smaller for other alcohols (*19*). Now it has been reported (*41*) that during the uv photolysis of liquid water containing isopropanol, in the presence of Pt + RuO_2 loaded TiO_2 sol, the quantum yield approached 1; this has been explained by electron injection from the isopropanol radical in the TiO_2 conduction band which multiplies the quantum yield by a factor of 2. If a heterolytic adsorption of isopropanol on the TiO_2 surface is assumed, a quantum yield of 1 could indeed be achieved:

$$(CH_3)_2CHOH_{(ads\,TiO_2)} \rightarrow (CH_3)_2CHO^-_{(ads\,TiO_2)} + H^+_{(ads\,TiO_2)} \quad [1a]$$

$$(CH_3)_2CHO^-_{(ads\,TiO_2)} + h^+ \rightarrow (CH_3)_2CO_{(ads\,TiO_2)} + H\ (\text{or } H^+ + e^-) \quad [3a]$$

Such a scheme accounts for the production of one H_2 and one acetone molecule with the help of only one electron-hole pair. For a homolytic splitting of isopropanol (Eq. [1]) a similar quantum yield of 1 could be achieved (no h^+ required):

$$(CH_3)_2CHOH_{(ads\,TiO_2)} \rightarrow (CH_3)_2CHO^{\cdot}_{(ads\,TiO_2)} + H\ (\text{or } H^+ + e^-) \quad [1b]$$

the positive hole being required for reaction [3] only. However, no evidence for such a high quantum yield is found for the dehydrogenation of alcohols in the absence of water (*19*).

(c) Photoproduced acetone is desorbed to the gas phase but it competes with isopropanol for the adsorption on TiO_2:

$$(CH_3)_2CO_{(ads\,TiO_2)} \rightarrow (CH_3)_2CO_{(g)} + TiO_2$$

according to a Langmuir competitive adsorption model. For low densities of Pt sites on the surface of TiO_2, step [2] is slower than steps [1] or [3]. The global reaction of photodehydrogenation of isopropanol in the adsorbed phase (step [2], or steps [1] and [3]) is, in both cases, the rate-determining step.

Finally, on Pt/TiO_2 catalysts, where Pt may be well dispersed (50%), irrespective of the loading, the kinetic behavior of the photodehydrogenation of isopropanol is very similar to that of the thermal dehydrogenation.

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