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Photocatalytic Isotopic Exchange between Cyclopentane and Deuterium over a Bifunctional Pt/TiO_2 Catalyst

H. COURBON, J.-M. HERRMANN, AND P. PICHAT

Institut de Recherches sur la Catalyse, 2 avenue Albert Einstein, 69626 Villeurbanne Cedex, France

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Cyclopentane–deuterium isotopic exchange (CDIE) was performed at −10°C with a C_5H_{10}/D_2 ratio of ≃6.4% over an illuminated (300–410 nm) 0.5 wt% Pt/anatase catalyst. A selectivity in C_5H_9D of ≃90% was found with a total quantum yield of ≃1.8%. The photocatalytic nature of CDIE under these conditions was established from these results: (i) no CDIE in the absence of photons of wavelengths shorter than the absorption edge of anatase or when TiO_2 was replaced by SiO_2, whereas the CDIE observed at higher temperatures (from 0°C) without uv light mainly produced multiply exchanged cyclopentane, (ii) a linear CDIE rate–illumination time relationship was found, and (iii) an experiment carried out with the same catalyst sample showed that it was capable of exchanging, in successive runs, without decrease in activity, an amount of C_5H_{10} 78 times greater than that corresponding to a photoinduced stoichiometric surface reaction. By contrast, CDIE over pure TiO_2 was limited and was only observed for hydroxylated specimens pretreated in D_2 at 300°C. It is concluded that (i) CDIE occurred on anatase between weakly adsorbed C_5H_{10} and OD^- ions activated by the trapping of photoproduced positive holes, and (ii) Pt, besides attracting the support-free electrons which decreased the recombination of electron–hole pairs, regenerated the titania OD^- ions after their isotopic exchange, which involved D_2 dissociative adsorption on the metal and subsequent migration of D atoms to the oxide. This constitutes an example of bifunctional heterogeneous photocatalysis.

INTRODUCTION

Up to now, heterogeneous photocatalysis has mainly been concerned with oxidations (*1–22*) or with oxygen surface reactions (*9, 10, 23–33*) carried out mostly on pure semiconductor oxides. However, a new field of reactions was recently opened, owing to the use of metals deposited on photosensitive supports as catalysts. In addition to their activity in oxidation of hydrocarbons (*34*) and inorganic ions (*35*), these solids photoassist uphill phenomena: hydrocarbon production via a "photo-Kolbe" process (*36*), carbon dioxide methanation (*37*), amino-acid photosynthesis (*38*), and above all water photodecomposition (*39–45*). Generally, platinum supported on titania was used, since Pt is one of the best metal catalysts for dissociating or recombining hydrogen or hydrogenated compounds, while TiO_2 offers the advantage of possessing an interesting photoresponse in the near uv, although $SrTiO_3$ seems preferable because of its electron affinity when water decomposition without external bias is sought. On the other hand, titania has simultaneously appeared in classical catalysis by metals as a nonconventional support which induced strong interactions with the metal as evidenced for noble metals (*46*), such as ruthenium (*47c*) or platinum (*48–50*), and for nickel (*47a, 47b, 51*).

The objective of the present work was to determine the respective roles of Pt and TiO_2 in photocatalytic reactions where H_2 participates either as a reactant or as a product. Cyclopentane–deuterium isotopic exchange (CDIE), which has been thoroughly studied over supported Pt in the dark (*52–57*), was chosen as a probe reaction. Our intention is to apply the knowledge thus obtained to investigate uphill reactions involving hydrogen for a possible chemical storage of photonic energy.

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EXPERIMENTAL

1. Apparatus

The cyclopentane–deuterium isotopic exchange (CDIE) was carried out in the static cell made of fused silica previously used for oxygen isotope exchange (*30, 31*). After introduction of the catalyst, this cell was glassblown to the vacuum line equipped with an oil diffusion pump (Edwards) ($p \simeq 10^{-7}$–10^{-8} Torr), metallic valves (Grandville Phillips), and a quadrupole analyzer (Riber QMM 17). A Philips HPK 125-W uv lamp, coupled with a water-circulating cuvette and with a 300 to 410-nm filter (Corning 7.60), was used to illuminate the thin layer of powder catalyst spread on the bottom optical window of the cell. The radiant flux was measured with a power meter (United Detector Technology, model 21 A) calibrated against a microcalorimeter.

2. Materials

Reactants. Pure-grade (Fluka) cyclopentane was twice vacuum distilled before admission into the gas line. Deuterium (Société Air Liquide) was 99.4% isotopically pure.

Catalysts. The Pt/TiO_2 catalyst was prepared by impregnating a nonporous anatase sample (Degussa, P 25; specific area 50 m^2 g^{-1}) with a 10% chloroplatinic acid solution to obtain a 0.5 wt% content in platinum. The impregnated sample was evacuated at 80°C for 2 h in an inclined rotating flask and dried in an oven at 120°C for 2 h. The resulting batch was then placed in a Pyrex tube flushed with N_2 while raising the temperature and reduced in a H_2 flow (35 cm^3 min^{-1}) at 480°C for 15 h. It was again flushed with nitrogen while being cooled to room temperature, and subsequently conserved in a glass vial until further use.

The platinum dispersion—or percentage exposed—corresponding to the ratio of surface Pt atoms to the total number of Pt atoms measured by chemical analysis, was determined by H_2 and O_2 chemisorptions and H_2–O_2 titrations. When the catalyst was reduced in H_2 at 200°C, all these methods were in good agreement and indicated a dispersion of 54%. This value was confirmed by electron microscopy which showed homodispersed platinum particles of ca. 20 Å. When the reduction temperature T_R was raised, a strong metal–support interaction was observed, the irreversible hydrogen uptake at room temperature decreasing from 6.5 μmol H_2 per gram of catalyst (T_R = 200°C) to 3.0 μmol (T_R = 300°C) and finally to zero (T_R = 500°C). Nevertheless, by varying the pretreatment temperature in deuterium from 100 to 300°C, we found no substantial difference in the CDIE results. However, a definitive conclusion on the effects of metal–support interactions on CDIE requires further experiments focusing on this point.

3. Procedures

For each CDIE experiment, the Pt/TiO_2 catalyst which had been exposed to air after its initial reduction was first evacuated *in situ* at room temperature for 3 h, then reduced and deuterated in 100 Torr of D_2 at 300°C for 1 h. After outgassing at 300°C (10^{-7} Torr) for 30 min, it was cooled to room temperature and the cell was placed in a bath whose temperature was monitored within ±0.1°C by a HS 60 Huber cryostat. The photocatalytic runs were performed at −10°C, since this temperature is insufficient for CDIE to occur in the dark. The surface was covered with pure D_2 (10^{-2} Torr) and then the reacting mixture was admitted onto the nonilluminated catalyst at a pressure of 20 Torr with a great excess of deuterium (94% D_2 vs 6% C_5H_{10}) to limit (i) the deactivation of the catalyst which might arise from the accumulation of carbonaceous deposits on the metal for hydrocarbon-rich gaseous mixtures (*54*), and (ii) the isotopic dilution due to HD or H_2 molecules formed by the reaction, since these molecules can react in competition with deuterium so that the measured rate of exchange would be smaller than the real one. Before each reaction run, a mass pattern of pure cyclopentane was recorded in the dark to determine the fragmentation corrections of the peaks. The mass spectra were scanned *in situ* during continuous illumination of the catalyst, a calibrated leak valve connecting the cell to the gas analyzer. Ionizing electrons at 70 eV were used. The exchange product distributions were corrected for natural ^{13}C content and equal ionization efficiencies were assumed for all $C_5H_{10-i}D_i$ isomers. The fragmentation peaks of deuterated molecules were corrected by affecting a coefficient of 0.85 to each C–D bond instead of 1 for C–H as in Refs. (*54, 55*).

RESULTS

The different $C_5H_{10-i}D_i$-exchanged molecules will be denoted D_i throughout the text. In particular, D_2 will designate $C_5H_8D_2$, except in the unambiguous case of the different equations where D_2 will be the normal formula for deuterium molecules.

1. CDIE over Illuminated Pt–TiO_2 Catalyst

As soon as the fixed catalytic bed, maintained at −10°C, was illuminated, the exchange of cyclopentane to D_1 species began. Figures 1 and 2A show that only traces of D_2 to D_5 were detected, but no D_6 to D_{10}, which excludes any rollover of the cyclopentane molecule as found for thermally activated catalysts (*53–57*). Moreover, D_2–D_5 molecules seemed to appear after an induction period (Fig. 1) which tends to show that they are not primary products. They probably correspond to subsequent adsorption periods of already-exchanged cyclopentane molecules as observed in Ref. (*58*). No cyclopentane and cyclopentadiene were obtained in contrast with CDIE carried out on pure titania at 700 K (*58*). The selectivity to D_1 $((d[D_1]/dt)/(d\Sigma[D_i]/dt))$ was ≃90% after illuminating for 1 h (21.5% exchange).

To determine, in particular, if the reac-

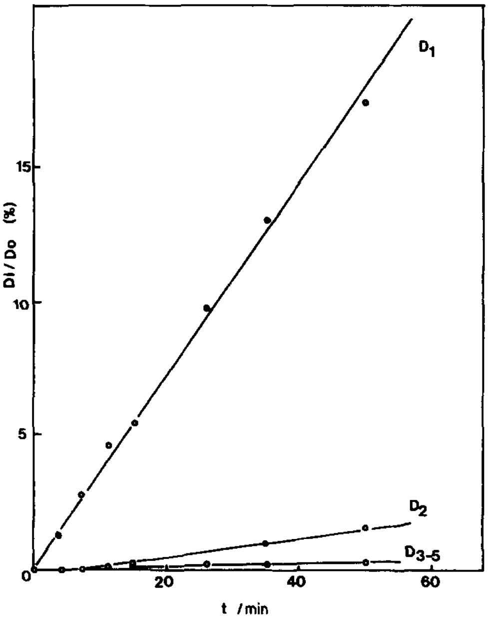


FIG. 1. Kinetics of D_i formation (in percent) over Pt/TiO_2 illuminated at −10°C.

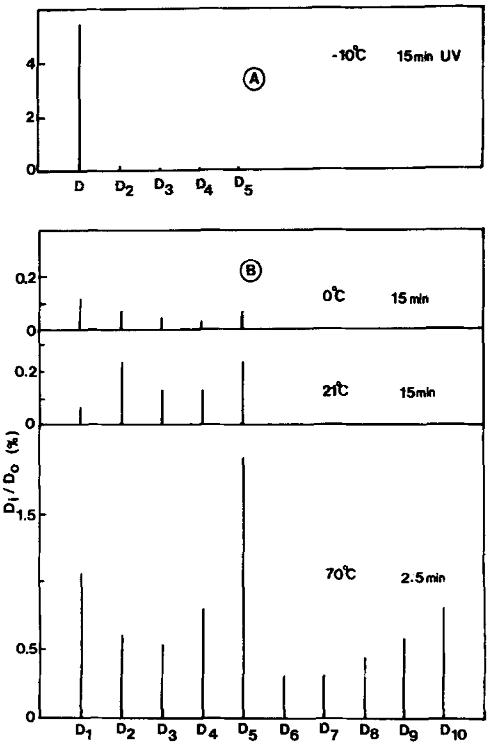


FIG. 2. Patterns of cyclopentane exchanged over Pt/TiO_2. (A) After 15 min of uv illumination at −10°C. (B) In the dark at 0, 21, and 70°C. The shorter time (2.5 min) for 70°C was chosen to get the smallest conversion possible to be compared with the other ones.

tion might be due to nonrenewable active surface species a prolonged CDIE experiment was carried out over the same Pt/TiO_2 sample. However, to avoid too high an isotopic dilution of D_2 into HD and H_2 due to the exchange, the experiment was divided into several uv-illumination periods of 1.5 h each, separated by an evacuation to 10^{-5} Torr for 15 min, followed by an introduction of a fresh reacting mixture. For these irradiation sequences, a linear photocatalytic activity–time relationship was found. This demonstrates that the photocatalytic reaction was not inhibited by a self-poisoning process. This absence of catalyst deactivation can be correlated to the experimental conditions based on a large excess in deuterium and a very low temperature. It also underlines that uv irradiation did not cause poisoning by a possible photocatalytic cracking of the hydrocarbon.

On the other hand, no substantial change in activity and selectivity was observed by changing the reduction pretreatment temperature in deuterium from 300 to 100°C.

Quantum yield. We define the quantum yield as the ratio of r, the number of cyclopentane molecules exchanged per unit of time and per unit of surface section of irradiated catalytic bed to the effective—i.e., absorbable by the anatase sample—photonic flux Φ_e relative to the same units. Φ_e was calculated by taking into account the spectral distribution of the lamp, the uv filter transmittance, the catalyst absorbance, and the radiant flux measured with the radiometer.

If we designate by

N_0 the initial number of cyclopentane molecules;

τ the conversion;

α the efficiency of absorbed photons for generating electron–hole pairs; it was assumed to be equal to 1;

P_0 the incident light power ($\simeq 3.0$ mW cm^{-2});

Φ the flux of effective photons per milliwatt of incident light power (with the optical system used, it was determined as equal to 1.20×10^{15} photons mW^{-1}) for our sample;

S the section area of the catalytic bed (9.6 cm^2);

η the ratio $(P_0 - P_T)/P_0$, which was found equal to 0.7, P_T being the transmitted light power;

R the reflectivity of the solid, equal to 0.15 from Refs. (*59*, *60*); the reflectivity of the Pt crystallites was neglected;

μ the fraction of TiO_2 surface occulted by the metal deposit (for a loading of 0.5 wt% of Pt and a dispersion of 0.54, μ corresponded to 3×10^{-3} and was therefore ignored),

the quantum yield ρ is given by

$$\rho = \frac{r}{\Phi_e} = \frac{N_0(d\tau/dt)}{\alpha P_0 \Phi S \eta (1 - R)(1 - \mu)}.$$

It was found to be equal to 1.6% for D_1 formation, while the global quantum for D_1–D_5 was close to 1.8%, referring to the first hour of illumination.

2. *Comparison of Catalytic and Photocatalytic CDIE over Pt/TiO$_2$*

In the absence of illumination, the rate of exchange was negligible at −10°C. It increased with increasing temperatures and multiply exchanged molecules were formed starting from 0°C, even for low exchange yields (Fig. 2B), as in the case of Pt/SiO_2 (*54*) and Pt/Al_2O_3 (*55*, *57*) catalysts. In particular, it can be seen that the rollover of the cyclopentane molecule started at a temperature between 21 and 70°C (Fig. 2B).

These results show that the illumination employed did not heat the catalyst, otherwise a multiple exchange would have been observed, even for a 10°C rise. This absence of thermal effect is in agreement with experiments on the photocatalytic dehydrogenation of alcohols carried out with illuminated suspensions of Pt/TiO_2 in alcoholic solutions where no temperature increase caused by illumination was found (*61*).

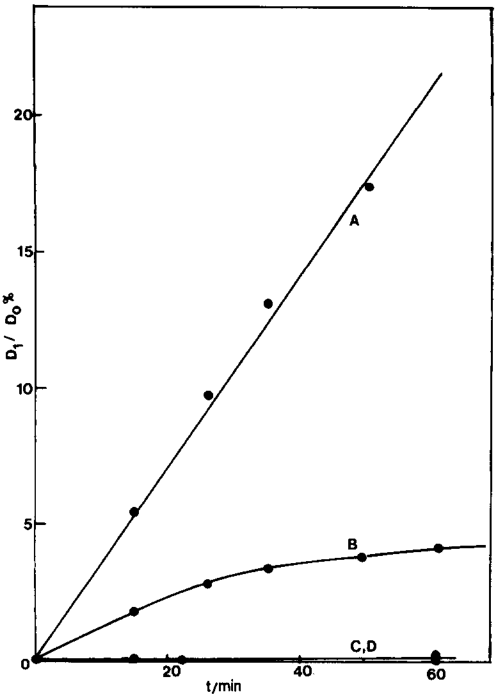


FIG. 3. Kinetics of CDIE on differently pretreated TiO_2 compared with (A) Pt/TiO_2; (B) sample pretreated in D_2 at 300°C; (C) sample pretreated in H_2 at 300°C; (D) dehydroxylated sample.

3. *CDIE over TiO_2*

To elucidate the respective roles of the metal and its support, CDIE experiments under illumination were performed at −10°C with the bare support which had undergone various pretreatments.

Pretreatment in D_2 as for Pt/TiO_2. A photoinduced exchange did occur and also produced mostly D_1, but at a smaller rate which additionally diminished as a function of time (Fig. 3, curve B) and tended to zero, whereas the reaction rate remained constant in the curve of the Pt/TiO_2 sample (compare curves B and A in Fig. 3).

Pretreatment in H_2. When deuterium was replaced by hydrogen as reducing agent in the above pretreatment, almost no CDIE was observed after introduction of the reacting mixture at −10°C over the sample carefully evacuated at 300°C (Fig. 3, curve C). On the contrary, this replacement of D_2 by H_2 for pretreating the Pt/TiO_2 catalyst had no significant effect on the subsequent CDIE.

Dehydroxylating pretreatment. CDIE was also cancelled if the anatase sample was previously dehydroxylated (calcination in 100 Torr O_2 at 450°C for 4 h, followed by an evacuation at the same temperature for 15 h) (Fig. 3, curve D).

4. *CDIE over Pt/SiO_2*

As metals were claimed to exhibit a photocatalytic activity (*62–64*) titania was replaced by silica. A Pt/SiO_2 catalyst (1.5 wt% of platinum with a dispersion of 40% on an aerosil (Degussa) of 200 $m^2\ g^{-1}$) described in Ref. (*65*) was used and no significant exchange was observed at −10°C, either in the dark or under illumination (300–410 nm as for the Pt/TiO_2 sample).

DISCUSSION

1. *Photocatalytic Nature of CDIE over Pt/TiO_2 at −10°C*

As in our other studies dealing with the oxidation of isobutane (*18*) and ammonia (*19*) or with the dehydrogenation of alcohols (*61*), experiments were undertaken to establish the real photocatalytic nature of the phenomena reported. In particular, they were conceived to show that (i) homogeneous photochemical reactions, due to the use of wavelengths capable of exciting the reactants or products, were negligible, and (ii) photoinduced stoichiometric reactions arising from surface or preadsorbed species could not account for the results as recently emphasized (*66, 67*).

In the present case, C_5H_{10} and D_2 do not absorb the wavelengths used and a blank experiment without catalyst corroborated the absence of CDIE.

As observed by using several optical filters, CDIE did not take place at −10°C in the absence of photons at least as energetic as the band gap of anatase (≃3 eV). The unsignificant activity at the same temperature of Pt supported on SiO_2, whose band gap is much wider than that of anatase, confirmed that the CDIE observed in the case of the Pt/TiO_2 catalyst originated from the interaction of TiO_2 with photons of suitable energy.

It should also be noted that an increase in temperature due to the conversion of light energy into heat by the platinum crystallites, acting as blackbodies and being consequently thermoactivated, would have led to multiply exchanged molecules in conformity with the results obtained for Pt deposited on titania starting from 0°C (Fig. 2B) in this study and on silica (*54*) or on alumina (*55–57*) for temperatures >55°C.

The key role of illuminated TiO_2 in the bicomponent Pt/TiO_2 catalyst was also demonstrated by a certain conversion in CDIE found for titania alone pretreated in D_2 at 300°C (Fig. 3, curve B). However, this activity tended to zero as a function of time and the exchange level reached probably corresponded to the exhaustion of surface species as discussed in the next section (an initial coverage of 0.6 species per square nanometer can be calculated if each species is assumed to exchange one molecule of cyclopentane).

On the contrary, CDIE over illuminated Pt/TiO_2 is not only more rapid (Fig. 3), but catalytic since (i) the rate of exchange against time is constant (Fig. 3, curve A), and (ii) the amount of cyclopentane molecules exchanged during repeated runs over the same sample (see under Results) was 78 times greater than the limit attained with TiO_2 alone pretreated under the same conditions (Fig. 3, curve B), which may be considered as corresponding to the achievement of a photoinduced stoichiometric exchange at the anatase surface.

2. *Mechanism*

As indicated above, the basic phenomenon is the absorption by TiO_2 of photons with an energy at least equal to the band gap energy, which creates electron–hole pairs near the surface:

$$(TiO_2) + h\nu \rightarrow p^+ + e^-. \qquad (1)$$

Since anatase already possesses an excess of free electrons which is still increased by the ionization of anionic vacancies arising from the reducing pretreatment at 300°C under deuterium (*68*), the minority charge carriers, i.e., the photoproduced holes p^+, are the limiting species involved in the photocatalytic process.

They are attracted to the surface because of the potential gradient in the depletion region. Because of coulombic forces, they probably react with negative surface or adsorbed species to which they transfer an activation energy symbolized by the asterisk:

$$A_s^- + p^+ \rightarrow A_s^*. \qquad (2)$$

The subscript s refers to surface entities. If CDIE is assumed to originate directly from this activation process, A_s^- should be deuterated. Two kinds of deuterated negative species can exist at the surface of TiO_2. In addition to deuterated hydroxyl anions OD^-, the existence of deuteride ions D^- might be considered since the reaction of a hydrogen atom with a Ti^{3+} surface cation to yield a Ti^{4+}–H^- configuration has been proposed from an electron-stimulated desorption study (*69*). However, the absence of CDIE over dehydroxylated TiO_2 indicates the importance of OD^- groups, formed during the deuterium pretreatment, as hole traps in the present case. Hole trapping by OH^- ions has been suggested in several articles (*3–8, 23, 24, 28, 33, 66*). Hence the equation

$$OD_s^- + p^+ \rightarrow OD_s^* \qquad (3)$$

should be considered as essential for CDIE over illuminated TiO_2 or Pt/TiO_2. A mechanism with D^- ions would proceed by hole neutralization as in Eq. (3). In the temperature range chosen cyclopentane is physically adsorbed on uv-irradiated titania as shown for alkanes (for example, a photogravimetric study of isobutane adsorption on uv-illuminated TiO_2 evidenced a weak reversible adsorption of the Langmuir type (*70*))

$$C_5H_{10\,g} \rightleftarrows C_5H_{10\,ads}. \quad (4)$$

In the following paragraphs, the subscript ads refers exclusively to titania and not to platinum. Consequently, because of the resulting coverage in cyclopentane, the probability of collision between $C_5H_{10\,ads}$ and activated OD* species is high enough to allow an isotopic exchange to take place,

$$OD_s^* + C_5H_{10\,ads} \rightarrow OH_s^{\cdot} + C_5H_9D_{ads} \rightarrow C_5H_9D_g. \quad (5)$$

The monodeuterocyclopentane then desorbs in the gas phase, while the hydroxyl radicals can restore their charge by capturing surface free electrons (*3*),

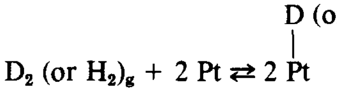
$$OH_s^{\cdot} + e^- \rightarrow OH_s^-. \quad (6)$$

This reaction accounts for the cyclic behavior of the process and the consumption of free electrons, thus decreasing the recombination rate with holes,

$$e^- + p^+ \rightarrow \epsilon. \quad (7)$$

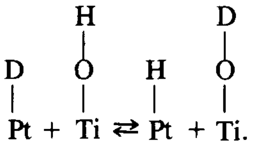
The energy produced, ϵ, can be dissipated either by reemission ($\epsilon = h\nu'$ with $\nu' \leq \nu$) or by excitation of the solid.

The OH^- ions produced on pure TiO_2 cannot exchange with gaseous deuterium at −10°C in the dark: infrared absorption bands of surface OD groups appear only after heating above 100°C and the detection of HD molecules in the gas phase requires an exchange temperature of at least 150°C (*71*). Moreover, we checked that illumination of TiO_2 in deuterium at −10°C did not affect the weak HD peak at $m/e = 3$. This explains (i) the inactivity of the TiO_2 sample pretreated in hydrogen at 300°C (Fig. 3, curve C), and (ii) the limited exchange obtained with that pretreated in deuterium (Fig. 3, curve B); after exchange of its OD groups formed during this initial pretreatment the bare anatase support could not regenerate them at the reaction temperature and therefore CDIE stopped. By contrast, in the presence of deposited Pt, OD groups can be produced at −10°C or even below, because of deuterium dissociative adsorption on platinum,



$$D_2\ (\text{or } H_2)_g + 2\,Pt \rightleftarrows 2\,\underset{\textstyle Pt}{\overset{D\ (\text{or } H)}{|}} \quad , \quad (8)$$

and of subsequent migration of D atoms from the metal to the support which enables isotopic exchange (*72–74*),

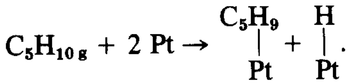


$$\underset{\textstyle Pt}{\overset{D}{|}} + \underset{\textstyle Ti}{\overset{\overset{H}{|}}{\underset{|}{O}}} \rightleftarrows \underset{\textstyle Pt}{\overset{H}{|}} + \underset{\textstyle Ti.}{\overset{\overset{D}{|}}{\underset{|}{O}}} \quad (9)$$

The rates of the forward and reverse reactions indicated by Eq. (8) are very fast on platinum group metals even at −78°C (*53*). Therefore, the presence of platinum on uv-irradiated TiO_2 makes the system work photocatalytically at −10°C by regenerating titania OD^- species (Eq. (9)) and by evolving, according to reaction (8), HD or H_2 molecules resulting from CDIE. On the other hand, the behavior of Pt is not markedly influenced by the temperature of the pretreatment in deuterium at least between 100 and 300°C. As this temperature change modifies the metal–support interaction (*46–51*) as shown by the H_2 irreversible uptakes (see under Experimental) and thence can affect the deuterium migration (spillover) between the metal and TiO_2, it may be inferred that this migration does not constitute the rate-limiting step of the photocatalytic CDIE. However, as already pointed out, a definitive conclusion on the effect of strong metal–support interactions requires a more complete experimentation.

The mechanism proposed accounts for the high selectivity in D_1 observed since cyclopentane is only weakly adsorbed on TiO_2 and consequently will not stay on the surface long enough to undergo a multiple exchange. This monodeuteroexchange is typical for saturated hydrocarbon exchange over thermally activated oxide catalysts such as chromia (*75*), titania (*58*) or activated $Mo(CO)_6/Al_2O_3$ (*76*). In the case of titania (*58*), monodeuteroalkanes were the only initial products, but the high selectivity in D_1 presently observed ($\simeq$90%) could not be reached because of concurrent dehydrogenation reactions due to the higher temperature. This mechanism corresponds to a monophotonic process since the absorption of one quantum gives rise to one activated OD* group which reacts with one adsorbed C_5H_{10} molecule.

In addition to its associative adsorption on titania (Eq. (4)), cyclopentane can adsorb dissociatively on platinum in the dark at −10°C:



$$C_5H_{10\,g} + 2\,Pt \rightarrow \underset{Pt}{\overset{C_5H_9}{|}} + \underset{Pt}{\overset{H}{|}}. \quad (10)$$

But the temperature is too low to make the reverse reaction which would produce D_1 without illumination possible. The occurrence of reaction (10) is corroborated by the production at −10°C before illumination of a small amount of HD molecules arising from Eq. (8), while the formation of D_1 species was not observed.

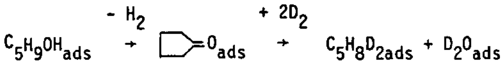
An alternative for Eqs. (3) and (5) could be proposed by suggesting the formation of atomic hydrogen (deuterium) from OH (OD) groups on uv-irradiated titania according to Ref. (*77*). No clear evidence for such a mechanism can be presented. In fact, the breaking of OD bonds is involved in reaction (5) but isotopic exchange can proceed through an associative mechanism. One may also consider the formation of hydrogen (or deuterium) peroxide which can decompose through a Fenton-like process and oxidize cyclopentane into cyclopentanol:

$$2\,OD^*_{ads} \rightarrow D_2O_{2\,ads} \xrightarrow{C_5H_{10\,ads}} D_2O_{ads} + C_5H_9OH_{ads}.$$

From this last intermediate, deuterated cyclopentane might be formed either by direct hydrogenation,

$$C_5H_9OH_{ads} \xrightarrow{D_1} C_5H_9D_{1\,ads} + HOD_{ads},$$

or via a cyclopentanone intermediate:



by analogy with the photocatalytic dehydrogenation of aliphatic primary and secondary alcohols on Pt/TiO_2 (*61*). On the basis of the following arguments, these reactions should be rejected: (i) although their detection is not easy because of the possibilities of adsorption on anatase, we found no evidence for the formation of C_5H_9OH, C_5H_8O, HOD, and D_2O in the mass spectra of the gas phase, (ii) the amount of $C_5H_8D_2$ formed was small and Fig. 1 shows that this compound probably resulted from the exchange of D_1, (iii) the regeneration of OD groups necessitates a rehydroxylation from HOD or D_2O which is not a truly reproducible process according to Refs. (*66, 71*), and (iv) it is difficult to envisage that the exchange occurred through an oxygenated compound in a reducing atmosphere.

CONCLUSIONS

Illuminated Pt/TiO_2 behaves as a dual-functional catalyst for CDIE. This exchange reaction does not take place on the metal but on its support activated by the photons. It involves weakly adsorbed C_5H_{10} molecules whose residence time at the surface is short, which accounts for the high selectivity in monodeuterated cyclopentane contrary to what is observed when CDIE occurs on the metal. Surface OD^- ions activated by photoproduced minority carriers (holes) are presumed to be responsible for the exchange. Owing to its dissociative properties toward deuterium, platinum renders CDIE catalytic by supplying deuterium atoms to anatase in order to replace those consumed by the reaction. This implies a deuterium migration (spillover) between the metal and its support, probably via hydroxyl groups. In addition, it should be emphasized that platinum is capable of removing electrons from the semiconductor as indicated in recent spectroscopic surface studies (*78*). This should favor the photocatalytic process by reducing the recombination between electrons and holes. Nevertheless the quantum yield ρ is much smaller than unity. We think that the main determining factor for ρ in these photocatalytic reactions is the reactivity between the reactant to transform and the photoactivated species. In the present case, the weak reactivity of physisorbed cyclopentane toward OD* groups (Eq. (5)) would explain the value obtained ($\simeq 1.8\%$), as well as the experimental conditions which have not been optimized.

Work is in progress to investigate the possibilities of such catalysts, constituted by a metal (or an alloy) exhibiting toward hydrogen the same properties as Pt and by a photosensitive semiconductor, in endoergonic dehydrogenation reactions which are of interest in the framework of chemical storage of light energy.

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