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Metal Content and Temperature Effects on the Photocatalytic Isotopic Exchange Cyclopentane–Deuterium over Pt or Ni/TiO_2 Catalysts in the "Normal" or "Strong Metal–Support Interaction" State

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A cyclopentane–deuterium isotopic exchange (CDIE) was carried out in gas phase, in the temperature range 228–273 K, using a static reactor with a fixed-bed layer of illuminated (300–410 nm) catalyst. Over Pt/TiO_2, an optimal temperature of about 260 K was found; at lower temperatures CDIE was limited by the hydrogen desorption from the metal crystallites; above 260 K the rate became dependent on the cyclopentane adsorption on TiO_2. At 260 K, an optimal content of about 0.5 wt% Pt, corresponding to ca. 1 Pt particle (homodispersed; ~2 nm diam, regardless of the content) per TiO_2 grain, was found for catalysts pretreated at 473 K in D_2 and containing 0.1 to 10 wt% Pt; beyond 0.5 wt% Pt, the detrimental recombination of the photoproduced charges at the Pt particles became apparent. Pt/TiO_2 samples pretreated at 773 K in D_2 showed the inhibition of CDIE by the so-called "strong metal–support interaction" (SMSI) effect as expected since reversible hydrogen chemisorption is required. Finally, CDIE also took place over Ni/TiO_2 samples where the metal was deposited as much larger particles (~15–18 nm diam); however, its rate was markedly reduced most likely because of the poorer interaction between the two catalyst components. These results are interpreted in terms of electronic exchanges and hydrogen spillover and substantiate the mechanism we proposed previously.

INTRODUCTION

Transition metals deposited on photoactive semiconductors increase the capabilities of these semiconductors for photocatalytic reactions. In particular they render catalytic at room temperature reactions involving hydrogen, such as the dehydrogenation of saturated (*1–11*) and unsaturated alcohols (*12, 13*), which might have an impact in organic synthesis. In a previous paper (*14*) we have shown the interest of the cyclopentane–deuterium isotopic exchange (CDIE) in gas phase to obtain information on Pt/TiO_2 catalysts and on their interaction with band-gap illumination. In the present brief article, the effects of various parameters (Pt content, pretreatment and reaction temperature, replacement of Pt by Ni) have been investigated to substantiate the mechanism of this reaction and thereby to improve our understanding of the role of both components of this type of photocatalyst. In addition, this isotopic exchange allows one to study the effect of the so-called "strong metal–support interaction" (SMSI) (*15–21*) whose existence was foreseen in Refs. (*22, 23*), since no oxygen-containing molecule, susceptible of canceling SMSI, is involved contrary to the case of alcohol dehydrogenation.

EXPERIMENTAL

1. Apparatus

The cyclopentane–deuterium isotopic exchange was carried out in the same fixed-bed photoreactor as was previously used (*14*). This reactor was connected to a Datametrics Barocel pressure sensor and to a quadrupole analyzer (Riber QMM 17). Illumination was provided by a Philips HPK

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125-W lamp through a water-circulating cuvette closed by a 300- to 410-nm filter (Corning 7.60) so that a mean radiant flux of 3.5 mW cm^{-2} reached the catalyst layer.

2. *Catalysts*

(*a*) *Pt/TiO_2*. They were prepared by adding a desired quantity of hexachloroplatinic acid solution to a stirred suspension of TiO_2 (Degussa P-25, 50 m^2 g^{-1}, mainly anatase), which was subsequently evacuated in a rotating flask at 353 K and dried at 383 K for 15 h. The powder was then reduced under flowing hydrogen at 753 K for 15 h. It was stored in a vial until further use. According to transmission electron microscopy (TEM), the Pt crystallites were present as well-homodispersed particles of ~2-nm diameter for metal contents between 0.1 and 10 wt%. Micrographs and size-distribution histograms have already been reported in detail (*2*). Determination of the Pt dispersion by H_2 and O_2 chemisorptions and reciprocal titrations confirmed these conclusions.

(*b*) *Ni/TiO_2*. The preparation was the same, nickel hexammine nitrate being used for the impregnation. TEM examinations were inconclusive to determine the particle size because of too small a difference between the Ni and TiO_2 particle sizes and because of a lack of contrast between the metal and its support. Magnetic measurements indicated that the mean size of the Ni particles was 15–18 nm for the 0.5 and 14 wt% loadings employed in this study.

3. *Procedures*

For each CDIE experiment, 100 mg of one of the prereduced M/TiO_2 catalysts was suspended in 4 cm^3 of distilled water. The slurry obtained was introduced into the photoreactor and dried by pumping, thus forming a thin layer of the catalyst without visible cracks on the bottom optical window. This layer absorbed about 95% of the incident radiant flux instead of about 70% in the case of a mere spreading of the same powder amount (*14*). The subsequent pretreatment included an evacuation at room temperature, a reduction in 13.3 kPa D_2 at 573 or 773 K for 1 h, and an outgassing (10^{-5} Pa) at the same temperatures for 1 h. For CDIE the photoreactor was immersed in a bath whose temperature was maintained constant within ±0.1°C by means of a HS60 HUBER cryostat.

The surface was covered by pure deuterium (1.33 Pa) before admission of the reacting mixture (total pressure, 2.13 kPa), which contains an excess of deuterium (molar ratio $D_2/C_5H_{10} = 3$), in order to limit (i) the isotopic dilution resulting from the generation of HD or H_2 molecules during the reaction and (ii) the possible formation of carbonaceous deposits on the metal (*24*). No reaction occurred in the dark at 260 K, which was chosen as the working temperature unless otherwise stated. The peak heights were corrected for fragmentation on the basis of the mass spectrum of pure cyclopentane.

RESULTS

Since the photocatalytic process is very selective in monodeuterocyclopentane (*14*), the conversions are represented by the molar percentage D_1/D_0, where D_1 and D_0 denote C_5H_9D and C_5H_{10}, respectively.

1. *Effect of Pt Content*

The photocatalytic conversions for the various Pt/TiO_2 catalysts as a function of time are shown in Fig. 1. The straight lines obtained indicate that the photocatalytic activities were constant within the experiment duration. These activities are plotted as a function of the Pt content in Fig. 2 (curve A) where an optimum content around 0.5 wt% appears.

2. *Effect of Pretreatment*

The same experiments were repeated with solids reduced at 773 K in D_2 instead of at 573 K (Fig. 3) in order to decrease the subsequent D_2 chemisorption at 260 K, i.e., to induce the so-called "strong metal–support interaction" effect (see Discussion

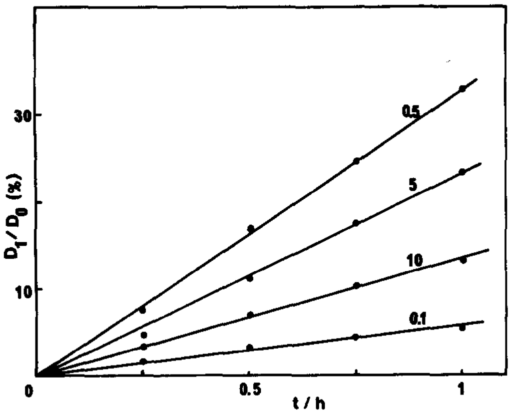

FIG. 1. Kinetics of the conversion of C_5H_{10} to C_5H_9D over various Pt/TiO_2 samples pretreated at 573 K and illuminated at 260 K. The numbers indicate the Pt content in wt%.

(*15–21*)). A neat decrease in activity was observed as may be seen when comparing Figs. 1 and 3 and curves A and B in Fig. 2. The solids with the lowest Pt contents were the most affected, to the extent that the 0.1 wt% Pt/TiO_2 sample cannot be distinguished from neat titania (pretreated at 573 K) at least for the first hour of illumination. The optimum at 0.5 wt% content does not exist any more and, finally, the 5 wt% Pt/TiO_2 sample is the most active (Fig. 2, curve B).

3. *Effect of Reaction Temperature*

CDIE was performed on the 5 wt% Pt sample (pretreated at 573 K) at various temperatures from 228 to 273 K, the temperature being raised in the dark between two successive runs. From the slopes dD_1/dt under illumination, the corresponding time-independent reaction rates were calculated and plotted in the Arrhenius diagram of Fig. 4, which shows a maximum around 260 K. For the lowest temperatures, the diagram parallels an asymptote, whose slope corresponds to an apparent activation energy of ~9 kcal mol^{-1} (~37.5 kJ mol^{-1}).

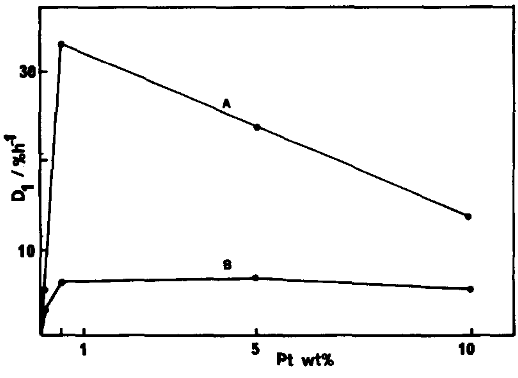

FIG. 2. Photocatalytic activities for C_5H_9D formation at 260 K as a function of Pt contents. Curve A: samples pretreated at 573 K ("normal" state); curve B: samples pretreated at 773 K ("SMSI" state).

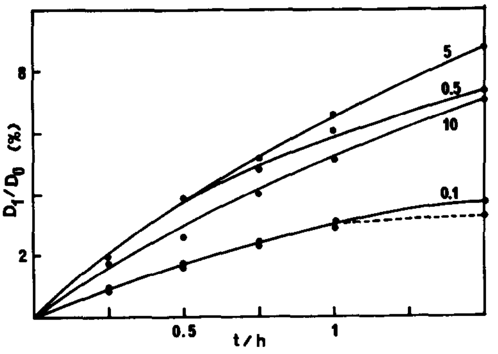

FIG. 3. Same as Fig. 1 for samples pretreated at 773 K ("SMSI" state). The dashed line refers to naked TiO_2 pretreated at 573 K.

4. *CDIE on Ni/TiO₂ Catalysts*

The results obtained with two samples are shown in Fig. 5. They indicate that (i) CDIE depended on the nickel content, (ii)

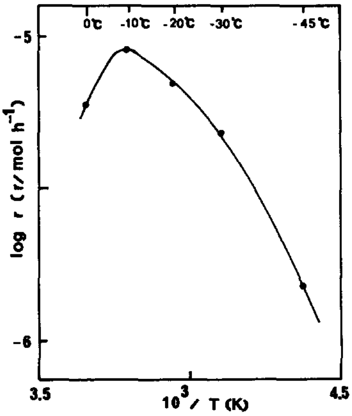

FIG. 4. Arrhenius plot of the photocatalytic activities for C_5H_9D formation over the 5 wt% Pt/TiO_2 sample pretreated at 573 K.

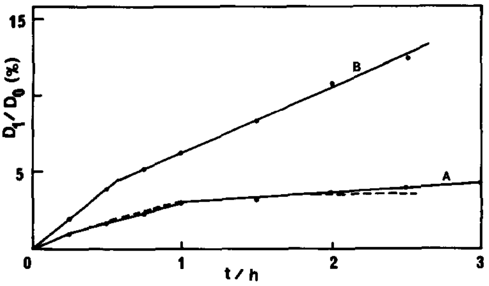

FIG. 5. Kinetics of the conversion of C_5H_{10} to C_5H_9D over Ni/TiO_2 samples pretreated at 573 K; curve A: 0.48 wt% Ni; curve B: 13.8 wt% Ni. The dashed line refers to naked TiO_2.

the activities were much lower than those of the Pt/TiO_2 samples, and (iii) the initial rate was higher than the mean one observed during the rest of the run. Curve B in Fig. 5 shows that this latter rate did not depend on the time within several hours (under conditions where the D_2/HD ratio remained high).

DISCUSSION

1. CDIE Mechanism

As proposed in previous papers (*14, 25*) it includes

—the creation of electron-hole pairs via band-gap absorption

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

—the dissociative adsorption of deuterium on platinum and the weak adsorption of cyclopentane on TiO_2

$$D_2(g) + 2\ Pt_s \rightleftarrows 2\ Pt_s - D \qquad (2)$$

$$C_5H_{10}(g) \rightleftarrows C_5H_{10}\ (ads); \qquad (3)$$

—the activation of surface OD_s^- groups by the photoproduced holes

$$OD_s^- + p^+ \rightarrow OD_s^*; \qquad (4)$$

—the isotopic exchange through an associative complex

$$C_5H_{10}\ (ads) + OD_s^* \rightarrow C_5H_9D\ (ads) + OH_s; \qquad (5)$$

and

—the regeneration of OD_s^- groups. This involves the spillover of deuterium (probably as deuterons) from the metal particles to the TiO_2 surface, reverse migration of hydrogen atoms (probably as protons) to the metal particles where they are desorbed principally as HD molecules, and capture of photoproduced electrons by the OD_s groups.

The effects of Pt content and of pretreatment studied here are consistent with this mechanism.

(*a*) *Effect of Pt content.* The initial increase of the rate with Pt content (≤0.5 wt%) can be easily explained by the fact that higher amounts of metal will favor D_2 dissociation and H_2 or HD evolution in the gas phase and accelerate the hydrogen spillover as well as the subsequent regeneration of deuteroxyl groups. But if the Pt particles had only this beneficial role, the reaction rate should increase with increasing Pt contents, possibly up to a limit. By contrast, the photocatalytic activity decreases markedly for Pt contents equal to 5 and 10 wt%. This cannot arise from a shading of TiO_2 by the metal particles since, for a 10 wt% Pt loading, only 6% of the support area is masked. The existence of a "structure-sensitive character" for CDIE observed for thermo-activated Pt/SiO_2 catalysts (*24, 26*) has to be ruled out since (i) all the Pt/TiO_2 samples have the same mean Pt particle size and (ii) the basic step of the reaction occurs on the support (Eq. (5)) and should not be too critically dependent on the metal dispersion provided it does not impede a good metal–semiconductor interaction. Finally, a back exchange cannot occur on the metal since (i) the isotopic dilution of H atoms is very high and (ii) the temperature is too low for a thermoactivated CDIE on Pt (see Experimental).

Because of their high electron density the Pt particles are capable of attracting the photoproduced holes and this effect, which increases with increasing Pt contents, is detrimental for the activation step represented by Eq. (4). In addition, photoconductance measurements under vacuum (*27*), as well as the determination of the amounts of photoadsorbed oxygen (*28*), have shown that the electron density of TiO_2 decreases as a function of the Pt content; this has been interpreted in terms of alignment of the Fermi levels of Pt and TiO_2, i.e., by an electron transfer from the semiconductor to the metal. In H_2 (or D_2) this transfer is diminished, as shown by the photoconductance which varies as $P_{H_2}^{1/2}$, because of hydrogen spillover from Pt to TiO_2 (*19*, *25*)

$$Pt_S{-}H + O_S^{2} \rightleftarrows Pt_S + OH_S^- + e^-$$

which is consistent with the decreased work function of Pt (*29–31*). Nevertheless, the Pt particles remain enriched in electrons, particularly for low Pt contents, and one can accordingly consider that they act as recombination centers for the photogenerated charges. The best compromise between the positive and negative effect of Pt with respect to the photocatalytic activity is obtained for a Pt loading of about 0.5 wt% (Fig. 2), which corresponds to approximately 1 Pt particle per TiO_2 grain. This latter ratio might arise from an optimum charge separation due to the electrical field created between the metal crystallite and the semiconductor grain.

(*b*) *Effect of pretreatment* (*"SMSI" state*). Pretreatment of M/TiO_2 catalysts in H_2 (D_2) at high temperatures modifies their chemisorptive properties toward H_2 and CO as well as their catalytic behaviors in various reactions (*15–23*) referring to a 573 K pretreatment. The resulting catalyst state has been designated as the "SMSI" state, whereas the 573 K pretreated catalyst is considered as being in the "normal" state. This does not mean that in this latter state there is no interaction between the metal and its semiconductor support. In particular, we have concluded that an electron transfer between the catalyst components occurs after a 473 K reduction (*19*) and even at room temperature under UV illumination (*27*).

CDIE is a favorable photocatalytic test reaction to observe SMSI effects since only hydrogen and hydrocarbon molecules are involved by contrast with, for instance, the photocatalytic dehydrogenation of alcohols for which the presence of oxygen-containing molecules will allow the reoxidation of the support and consequently suppress, at least partially, this phenomenon.

Figure 2 (curve B) shows that CDIE on Pt/TiO_2 is markedly inhibited by SMSI. Previous results obtained by other authors (*15–18*) and in our laboratory for the present samples have evidenced that H_2 (or D_2) chemisorption is decreased by SMSI and can even be canceled for low Pt loadings (*19*, *20*) within the limits of experimental accuracy. As a result the regeneration of OD groups at the surface of TiO_2 which involves deuterium spillover should be restrained and consequently CDIE should be affected. An additional effect is the dehydroxylation of the TiO_2 surface by treatment at 773 K. However, the existence of CDIE for Pt contents greater than 0.1 wt% indicates the possibility of at least a partial rehydroxylation of TiO_2 owing to deuterium atoms spilled over from the metal particles. Furthermore, the 0.5 wt% Pt/TiO_2 sample exhibited an activity comprised between those of the 5 and 10 wt% Pt/TiO_2 samples, although the amount of chemisorbed D_2 was virtually nil. Also note that the 0.5 wt% Pt/TiO_2 catalyst reduced at either 373 or 573 K had about the same activity, despite H_2 chemisorbed amounts differing by more than twofold. These facts might be due to the better charge separation previously invoked for this sample. However, on the whole, a decrease in D_2 chemisorption, induced by the 773 K pretreatment, caused a decrease in CDIE rate (Fig. 2).

2. *Effect of Reaction Temperature*

The Arrhenius plot of Fig. 4 can be divided into three regions and interpreted as follows.

(*a*) *Low temperatures* (*$288 \le T \le 253$ K*). The reaction is thermoactivated with a positive apparent activation energy E_a of ~9 kcal mol^{-1}. Since the activation of OD_s^- species by the photoproduced holes (Eq. (4)) is not thermoactivated, the true activation energy E_t must be nil. As the reaction temperature decreases, the rate-limiting step would be constituted by the desorption of HD (or H_2) from the metal crystallites:

$$E_a = E_t + Q_{H_2} = Q_{H_2} \simeq 9 \text{ kcal mol}^{-1}, \quad (6)$$

where Q_{H_2} is the heat of hydrogen reversible adsorption. The value of Q_{H_2} thus derived is equal to that found in the same temperature region and over the same catalysts for the photocatalytic alcohol dehydrogenation in the liquid phase (*2*). It is also equal to the experimental value determined by microcalorimetry on these samples (*32*) and to that reported for Pt/Al_2O_3 catalysts (*33*), thus confirming that hydrogen evolves from the metal and not from the photosensitive support.

(*b*) *Optimal temperature* (T_{opt}). The Arrhenius curve shows a maximum for ~260 K. The desorption of hydrogen is no longer the rate-limiting step. Such an optimal temperature is of fundamental importance since it defines the best working conditions for the photocatalyst, i.e., the best quantum yield (ratio of the reaction rate in molecules s^{-1} to the illumination flux in photons s^{-1}).

(*c*) *Temperatures >260 K*. Above T_{opt}, a negative term related to the heat of adsorption of cyclopentane Q_c intervenes in E_a:

$$E_a = E_t - \alpha_c Q_c < 0$$

with α_c tending to 1 as the temperature increases. The overall reaction rate becomes limited by the adsorption of cyclopentane on titania. Since this adsorption is of a weak associative type as for isobutane (*34*), this can explain why T_{opt} found for CDIE is smaller than that found for the alcohol dehydrogenation (313 K) since the adsorption of the alcohols on TiO_2 is of a stronger type (dissociative adsorption on basic sites of titania).

3. *Comparison between the Ni/TiO_2 and Pt/TiO_2 Samples*

The two Ni/TiO_2 samples show that nickel can play the same role as platinum. However, as in the case of the dehydrogenation of alcohols, these samples exhibit a lower activity than the Pt/TiO_2 specimens regardless of the metal content, despite the fact that a same weight percentage corresponds to about three times more Ni atoms than Pt atoms. Although distinct properties of these metals for deuterium dissociation and spillover can intervene, this is most probably related to the much larger Ni particles and accordingly to their poorer interaction with the TiO_2 grains as a whole.

The higher initial activities for both Ni/TiO_2 samples can be explained as follows. Since Ni/TiO_2 has a low activity—maybe related to the low Ni dispersion—the part of CDIE due to the fresh support is comparatively important as shown by the dashed curve in Fig. 5 which is relative to naked TiO_2. However, when the photoactivable OD_s^- groups initially present on naked TiO_2 are exhausted (for times >1.5 h under these conditions), the intrinsic activity of TiO_2 becomes nil. Consequently, if one subtracts the dashed curve from curves A and B in Fig. 5, one gets straight lines, originating from point 0, which corresponds to the constant intrinsic activities of the Ni/TiO_2 samples.

CONCLUSION

The present results dealing with CDIE are consistent with those previously obtained for the photocatalytic dehydrogenation of alcohols over the same solids (*1, 2, 9*). In both cases optimal temperature and metal content have been observed, as well as a greater efficiency for small supported Pt particles than for large Ni particles. This substantiates our previous conclusions: (i) both reactions involve reversible hydrogen spillover between the metal and the semiconductor of the bifunctional photocatalyst; (ii) H_2 (or HD) desorption from the metal crystallites can limit these reactions at low temperatures; (iii) the optimal metal content results from recombination of the photoproduced charges at the metal particles. Moreover, CDIE allows one to show an effect of SMSI upon the kinetics of a reaction carried out below room temperature and under illumination. This confirms the interest of CDIE as a test photocatalytic reaction, since, in addition, differences in selectivity between thermal and photonic activation enable one to employ it in order to determine whether a given illumination increases the temperature of a M/TiO_2 fixed bed (*14*, *35*). Finally, the extension of this isotopic exchange to appropriate molecules might be useful when a monodeuteration is desired.

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