Investigation of the Mechanism of Photocatalytic Alcohol Dehydrogenation over Pt/TiO₂ using Poisons and Labelled Ethanol

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Poisoning experiments using pyridine, piperidine, aqueous ammonia, phenol and 2-nitrophenol show that both acid and base sites are involved in the room-temperature photocatalytic dehydrogenation of alcohols (liquid propan-1-ol being chosen for the tests) over a Pt/TiO_2 catalyst. The dominant role is played by the base sites, since an acid of the strength of 2-nitrophenol suffices to cancel dehydrogenation, whereas the basic substances only decrease its rate. An additional piece of information on the dehydrogenation mechanism is obtained from the use of gaseous 2,2,2-[^aH₃]ethanol at 263 K which provides evidence that the β -deuterium atoms are not abstracted, whereas at 295 K an isotopic exchange between the products, H₂ and 2,2,2-[^aH₃]ethanal, subsequently occurs.

Saturated¹⁻¹⁶ and unsaturated^{17, 18} alcohols are efficiently dehydrogenated at room temperature under various conditions (gas or liquid phases or aqueous solutions) by heterogeneous photocatalysts formed from transition metals deposited on semiconductors. This dehydrogenation reaction, which appears as a very convenient test for these types of photocatalysts, might be of interest in organic synthesis and perhaps in the production of hydrogen and aldehydes from alcoholic solutions formed in fermentation processes. The following steps have been suggested for the dehydrogenation mechanism over titania supporting metals^{1, 2, 9} (the most frequently studied photocatalysts).

Creation of electron-positive hole pairs:

$$(\text{TiO}_2) + h\nu \rightarrow e^- + p^+ (h\nu \ge \text{TiO}_2 \text{ band gap}).$$
 (1)

Dissociative adsorption of the alcohol on the semiconductor basic sites:

$$CHOH \rightarrow CHO^- + H^+.$$
 (2)

Abstraction of a second hydrogen atom from the resulting alkoxide ion *via* reaction with a photoproduced hole (possibly as electron-deficient activated surface species):

$$CHO^{-} + p^{+} \rightarrow C = O + H^{-} \text{ (or } H^{+} + e^{-}\text{).}$$
 (3)

Formation and desorption of hydrogen, principally at the metal particles, owing to hydrogen spillover:

$$\mathbf{H}^{+} + \mathbf{e}_{\mathbf{M}}^{-} \to \mathbf{H}^{-} \to \frac{1}{2}\mathbf{H}_{2}.$$
 (4)

This was consistent with the effects of various parameters (light flux and wavelength, temperature, metal nature and content, metal particle size, nature and concentration of the alcohol), as well as with photoconductance measurements.^{9, 19}

We have undertaken this study to investigate this mechanism further. First, we utilized molecules indicating the role of surface base and acid sites; the use of poisons, although commonly employed in catalysis, has rarely²⁰ been reported in the case of photocatalytic

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reactions for which energetic levels of the semiconductor and of the reactant(s) are often predominantly considered with regard to the probe of active surface sites. Secondly, the dehydrogenation of CD_3CH_2OH has been examined to assess whether the β -hydrogen atoms are involved.

Experimental

The Pt/TiO₂ photocatalysts were prepared by impregnation with H_2PtCl_6 and reduction in H_2 of a Degussa P-25 sample as previously described.¹ The mean diameter of the Pt particles was 2 nm.² Reagents of purissimum grade were employed. Ethanol (2,2,2-[²H₃], 98%) containing *ca.* 5% water was purchased from Cambridge Isotope Lab. (USA) and subjected to freeze-thaw cycles before admission into the photoreactor.

For poisoning experiments, the liquid-phase static photoreactor, containing the stirred suspension of the 5 wt% Pt/TiO₂ catalyst in propan-1-ol (and various amounts of acidic or basic compounds), was a thermostatted flask with a Pyrex optical window. It was closed by a valve and connected to a rotatory vacuum pump and to a gas chromatograph for determination of the amount of H₂ formed. Before illumination, the suspension was deaerated several times using the pump; no oxygen was then detected by gas chromatography.

For the experiments with labelled ethanol, the gas-phase static photoreactor, containing on its bottom fused silica optical window a thin layer (obtained by evaporating an aqueous suspension) of 1 wt % Pt/TiO₂ catalyst, was a cylindrical box integrated into a greaseless vacuum line and connected to a quadrupole gas analyser, *via* an adjustable leak valve, and to a barocel pressure sensor. The sample was first evacuated (*ca*. 10⁻⁵ Pa) at 423 K for 16 h and then cooled to the reaction temperature [monitored by a thermostat (Huber H.S.40)].

In both types of experiment a Philips HPK 125 W mercury lamp was employed. The frequency range was limited by a circulating-water cuvette and by a Pyrex filter or optical window. The radiant flux received by the catalyst was ca. 38 mW cm⁻² (suspension) or ca. 4 mW cm⁻² (layer).

Under these conditions, the dehydrogenation of ethanol and propan-1-ol, as well as of other alcohols, has been demonstrated to be photocatalytic over the Pt/TiO_2 samples used.¹

Results and Discussion

Effects of Bases

The 5 wt% Pt/TiO₂ photocatalyst was dispersed in distilled water and stirred for 25 min. After filtration, it was evacuated (*ca.* 1.33 Pa) to remove most of the water. Finally, it was treated at 423 K, first in flowing N₂ for 3 h, then in flowing H₂ for 2 h, using flow rates of 35 cm³ min⁻¹. It was kept in a vial without avoiding exposure to air.

Three nitrogen-containing bases of different strengths, whose interactions with acid solids are well documented, have been chosen. Fig. 1 shows the effects of various quantities of pyridine or piperidine on the amounts of hydrogen produced from propan-1-ol using this photocatalyst. Pyridine concentrations in the range 3×10^{-4} to 3×10^{-3} mol dm⁻³, which correspond to *ca*. 1 to 10 molecule nm⁻² assuming total adsorption, decreased the dehydrogenation rate. However, the decrease was small. For larger amounts of pyridine (10 vol %, *ca*. 1.13 mol dm⁻³), a somewhat more substantial decrease was found, but the dehydrogenation reaction was still important; after illuminating for 1 h, the amount of hydrogen produced was divided by a factor of *ca*. 2 under the conditions of fig. 1. As expected, with piperidine, which is a stronger base (pK_a ≈ 11.2, *cf*. 5.23 for pyridine in aqueous solutions), the effect was much more

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Fig. 1. H₂ generated for suspensions of 70 mg 5 wt% Pt/TiO₂ in 20 cm³ propan-1-ol (*a*), with the addition of 0.5×10^{-3} cm³ pyridine (*b*), 1 cm³ pyridine (*c*), 0.1 cm³ piperidine (*d*), 1 cm³ piperidine (*e*).

pronounced (fig. 1). Also, note that hydrogen can be abstracted from piperidine as from other amines.

In another set of experiments, the photocatalyst was dispersed in a 50/50 vol% mixture of propan-1-ol with either water or 1 mol dm⁻³ NH₄OH (p $K_a \approx 9.24$). The presence of NH₄OH decreased the amount of hydrogen produced, for instance, about half as much hydrogen was generated after 1 h. Similarly, a mere pretreatment of the photocatalyst in 1 mol dm⁻³ NH₄OH instead of pure water (*vide supra*) reduced the H₂ formation slightly (fig. 2).

Effects of Acids

Phenol, whose adsorption on TiO₂ has been studied previously,²¹ has been chosen as well as 2-nitrophenol because of its higher acid strength. The addition to propan-1-ol of a quantity of phenol $(3.7 \times 10^{-3} \text{ mol dm}^{-3})$, equal to *ca*. 10 times the amount required for a coverage of the TiO₂ surface by 2 molecule nm⁻², decreased the hydrogen production (fig. 3). The effect was greater than that of $3.1 \times 10^{-3} \text{ mol dm}^{-3}$ pyridine and even slightly greater than that of $0.125 \text{ mol dm}^{-3}$ pyridine (fig. 1 and 3). Similarly, the initial effect of 0.1 mol dm⁻³ phenol was much greater than that of 1.13 mol dm⁻³ pyridine, although for longer illumination times the rates of H₂ production became comparable. A small

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Fig. 2. H_2 generated for suspensions of 70 mg 5 wt% Pt/TiO₂ in 20 cm³ propan-1-ol: sample pretreated in $H_2O(a)$ or in 1 mol dm⁻³ NH₄OH (b); with the addition of 10 cm³ H₂O (c) or 10 cm³ 1 mol dm⁻³ NH₄OH (d).

concentration $(2.8 \times 10^{-3} \text{ mol dm}^{-3})$ of 2-nitrophenol $(pK_a \approx 7.17 \text{ instead of } ca. 9.89 \text{ for phenol in aqueous solution})$ completely stopped the hydrogen formation (fig. 3).

Active Sites required for the Dehydrogenation

Acid and base sites exist at TiO_2 surfaces as evidenced by i.r. studies^{21a} and other methods^{21b} using adsorbates capable of donating or accepting protons or electron pairs. In addition, the platinum deposit increases the TiO_2 acidity.^{21c} In the preceding paragraphs, pK_a values have been indicated only as a rough guide, since they are no more valid to precisely predict the strength of interaction between a solid and acids or bases in the gaseous phase^{21d} or diluted in an organic liquid as in the present case.

The poisoning experiments show that both base and acid sites are involved in the dehydrogenation reaction. The essential role of base sites is underlined by (i) the greater influence of phenol compared with that of pyridine at equivalent concentrations and (ii) the complete inhibition found when using an acid of sufficient, although moderate, strength such as 2-nitrophenol. This is consistent with eqn (2), which presents the abstraction of the alcohol hydroxylic hydrogen atom on surface base sites as a prerequisite for dehydrogenation.

Total inhibition of gaseous propan-2-ol dehydrogenation over illuminated ZnO by

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Fig. 3. H₂ generated for suspensions of 70 mg 5 wt% Pt/TiO₂ in 20 cm³ propan-1-ol (a), with the addition of phenol $(3.7 \times 10^{-3} \text{ mol dm}^{-3})$ (b), $(0.1 \text{ mol dm}^{-3})$ (c) or of 2-nitrophenol $(2.8 \times 10^{-3} \text{ mol dm}^{-3})$ (d).

preadsorbed acetic acid and phenol has previously been observed, and from experiments allowing the measurement of the amounts of propan-2-ol adsorbed in the dark, it was concluded that these acidic compounds prevent the irreversible adsorption of the alcohol.²⁰ This conclusion is in agreement with eqn (2). However, phenol did not suppress dehydrogenation over TiO₂ in contrast with what was reported for ZnO.²⁰ Apart from a possible effect of different experimental conditions, this can easily be explained by the less basic character of the TiO₂ surface. Indeed, an infrared study^{21a} has shown that gaseous phenol interacts only weakly with hydroxylated TiO₂, unlike acetic acid.

Phenols and chlorophenols in aqueous solutions are degraded over illuminated TiO_2 . However, O_2 and H_2O are needed. Furthermore, if such a mineralization had occurred under the present conditions, the dehydrogenation rate would have increased progressively because of the phenol disappearance, which was not the case (fig. 3), and the great difference observed between phenol and 2-nitrophenol would not have been observed.

The inhibition due to phenol or 2-nitrophenol might also arise from a poisoning of the Pt catalytic properties by adsorption of these molecules *via* their π electrons on the supported metal particles. However, as the inhibition is not complete in the case of phenol, the hydrogen produced by dehydrogenation should be capable of hydrogenating the phenol adsorbed on the platinum, thereby decreasing its adsorption, which in turn would increase the dehydrogenation rate, in contrast with the present results (fig. 3).

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Consequently, the poisoning of the TiO_2 base sites is certainly the main phenomenon which accounts for the inhibiting effect of the acidic adsorbates.

Acid sites can play a role either in the adsorption of the alkoxide species and thereby in the dissociative adsorption of the alcohol [eqn (2)] or in the abstraction of a hydrogen atom from the alkoxide species [eqn (3)] or in both processes. For thermally catalysed dehydrogenation, abstraction of a hydride ion from alkoxide species on acid sites of hydroxyapatite catalysts²² and of chromia²³ has been suggested. In the present case, the participation of photoproduced holes [eqn (3)] would result in the abstraction of a hydrogen atom in place of a hydride ion; however, acid sites could also be involved. In addition, impregnation of the photocatalyst by NH₄OH can restrain the alcohol dissociative adsorption [eqn (2)] because of the competitive adsorption of protons and ammonium ions on TiO₂.

Moreover, bases such as pyridine and piperidine are known to poison Group VIII transition-metal catalysts. Accordingly, the influence we observed cannot be interpreted unambiguously since both the properties of TiO_2 and of the Pt particles can be affected. A more precise understanding of the inhibiting effect of bases on dehydrogenation must, therefore, await other data. Nevertheless, this effect is much less pronounced than that of acids as already emphasized.

On the other hand, a beneficial effect of NaOH or KOH on the generation of hydrogen from gaseous²⁴⁻²⁷ or liquid²⁸⁻³² water over various illuminated doped or undoped semiconductors supporting metals such as TiO_2 ,^{24-28, 32} Sr-TiO₃,^{27, 30, 31} NiO-SrTiO₃²⁹ and iron oxides³⁰ has been attributed, at least in part, to the increased surface coverage by OH⁻ ions (the dependence of the semiconductor flat-band potential upon the pH being also invoked for liquid water). The decreased hydrogen production from propan-1-ol we found can be ascribed to the competition between OH⁻ ions and alkoxide species [eqn (3)] for hole capture.

Dehydrogenation of CD₃CH₂OH

At 263 K, the illumination of Pt/TiO₂ equilibrated in the dark with the vapour pressure of this labelled alcohol resulted in phenomena caused by the expected dehydrogenation: pressure increase, growths of the mass-2 peak due to H₂, and of the mass-47 peak to which the parent peak of CD₃CHO contributes. The mass-3 peak referring to HD molecules increased, but the ratio of this peak to that at mass 2 remained quite small: ca. 2.5% within the first two minutes with a very low accuracy because of the small height of the HD peak; ca. 1.5% after illuminating for 150 min, having thus generated ca. 1.3×10^{-4} mol of hydrogen.

In addition, (i) the ratio of the mass-49 peak (parent ion of CD_3CH_2OH) and of the 48 peak (parent ion of CD_2HCH_2OH if it were formed), and (ii) allowing for the adequate fragmentation corrections, the ratio of the peaks at mass 47 (parent peak of CD_3CHO) and at mass 46 (parent peak of CD_2HCHO if it were produced) remained constant for ionizing potentials of 10 or 70 eV.

The absence of variation of these three ratios (m/e = 3:2; 49:48; and 47:46) undoubtedly shows that the deuterium atoms of the methyl group of the labelled ethanol used are not abstracted during the dehydrogenation at 263 K, in agreement with eqn (2) and (3).

When Pt/TiO₂ exposed to CD₃CH₂OH was illuminated at 295 K, instead of 263 K, the observed phenomena were initially the same. However, as the H₂ pressure increased, the ratio HD/H₂ also increased considerably (fig. 4), although the successive increments of H₂ dominated those of HD. Gaseous deuterium also appeared and the D₂/HD ratio became progressively greater. At the same time, no significant change was found in the ratio of the mass-49 and mass-48 peaks (ionizing potential: 10 eV), *i.e.* CD₂HCH₂OH molecules did not form. By contrast, the ratio of the peaks, corrected for CD₃CH₂OH

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Fig. 4. Variations of the ratios HD/H₂ (a) and D₂/HD (b) during the illumination of 1 wt% Pt/TiO₂ exposed to gaseous 2,2,2-[²H₃]ethanol at 295 K in a static reactor.

fragmentation, at mass 47 and mass 46 progressively decreased, indicating the appearance of CD_2HCHO molecules. This was corroborated by the decrease of the ratio of the 47 and 45 peaks.

These results can be interpreted as follows. The dehydrogenation does not involve the deuterium atoms of the labelled ethanol, which generates H₂. This was the sole reaction noticeable within the first 5 min under the conditions used. Then an isotopic exchange between the dehydrogenation products, CD₃CHO and H₂, took place, as shown by the behaviour of the 3, 4, 46 and 45 peaks. For Pt/TiO₂, multiple isotopic exchange between cyclopentane and an excess of deuterium has been reported to occur on the Pt particles at temperatures ≥ 273 K in the dark, whereas illumination at temperatures below 273 K resulted in monoexchange.³³ Other hydrocarbons can obviously be exchanged under the same conditions, as shown by current studies dealing with propane. In the present case, because of both the weak pressure of H_2 and the preponderance of the photocatalytic dehydrogenation of ethanol for which a much greater quantum yield has been found, the photocatalytic isotopic exchange, although slightly activated, is certainly negligible as shown by the experiments at 263 K. The activated isotopic exchange, which occurs despite the unfavourable pressure and temperature conditions, concerns the CD₂CHO molecules, very likely because it is facilitated by the equilibrium with the enolic form $CD_2 = CHOD$ (tautomerism).

Conclusion

This study demonstrates that the β -hydrogen atoms of an aliphatic alcohol, such as ethanol, are not involved in the primary steps of the room-temperature photocatalytic dehydrogenation over Pt/TiO₂. It also shows that the titania base sites are essential; this is consistent with the proposal that the active alcoholic species are the alkoxide ions resulting from the abstraction of the hydroxylic hydrogen atoms on these sites. The interpretation of the inhibiting effect of basic compounds is not so straightforward, since poisoning of both metal sites and oxide acid sites can intervene; however, this latter type of site is likely to be required for the dehydrogenation, *i.e.* the amphoteric character of the TiO₂ surface is implicated.

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