

Short Communication

The effects of the addition of alcohols or ethers on the photolysis of the *n*-butyl-*o*-titanate-water system

T. SHINODA

National Chemical Laboratory for Industry, Tsukuba Research Centre, Yatabe, Ibaraki 305 (Japan)

K. OHKAWA

Training Institute for Environmental Pollution Control, Namiki 3-3, Tokorozawa, Saitama 359 (Japan)

(Received December 1, 1982; in revised form January 12, 1983)

1. Introduction

The photolysis of water by sunlight has recently been studied extensively in order to find new energy resources. Studies of the photolysis of water over TiO_2 at the gas-solid interface have been reported by a number of workers [1]. We have performed a similar investigation of the photocatalytic effects of the solid obtained by evaporating the solvent from a mixture of silica gel and an *n*-butyl-*o*-titanate ($\text{Ti}(\text{OBu})_4$)-benzene solution. When a small quantity of an alcohol or an ether was added, it was found that the amount of hydrogen gas produced increased by a factor of about 10. This effect may be different from that reported by Sakata and Kawai [2] for the photolysis of water over TiO_2 . In the present case it is possible that a titanium(IV) complex is formed by direct reaction between polymerized *n*-butyl-*o*-titanate and the alcohol or ether added to the benzene solution [3].

2. Experimental details

5.5 g of white silica gel (SiG) (Koso Chemicals) was used as the carrier for one charge in the reaction tube. The particle diameter was between 2 and 3 mm. 0.5 g of $\text{Ti}(\text{OBu})_4$ monomer (Tokyo Kasei Industries Ltd.) was dissolved in about 10 ml of benzene, mixed with the SiG and coated onto it with simultaneous polymerization by evaporating the solvent at room temperature. For convenience this mixture is hereafter designated as the untreated catalyst. The alcohol or the ether was added to about 20 ml of the benzene solution. After evaporation of benzene the catalyst was transferred to a transparent silica tube with an external diameter of 10 mm. Water-saturated nitrogen gas at a temperature of 60 °C was passed through the reaction tube which was illuminated using a Toshiba mercury lamp H400-P (400 W). The linear flow rate of nitrogen was 99 cm min^{-1} . After 10 min

illumination, the gas at the exit of the reaction tube was analysed by gas-liquid chromatography. Two Ohkura model 701 gas chromatographs were used under the following conditions: column, 3 mm \times 2 m; Porapak-Q and molecular sieve 5A respectively; temperature, 120 $^{\circ}$ C and 80 $^{\circ}$ C respectively; carrier gases, nitrogen and helium respectively at a flow rate of 40 ml min^{-1} . After 15 min the illumination was repeated. The IR spectrum of the gas produced by the reaction was obtained in the region from 650 to 4000 cm^{-1} using an IR spectrophotometer (model A-102, Japan Spectroscopic Co. Ltd.).

3. Results and discussion

The retention times and IR bands observed for the catalysts indicate that the same gaseous species are produced by the alcohol-treated catalysts, the ether-treated catalysts and the untreated catalyst; however, the hydrogen yield was increased when the treated catalysts were used. When more alcohol or ether was added, CH_4 and CO_2 were produced on illumination and the hydrogen yield decreased. The CH_4 and CO_2 peaks were identified using a reference gas. This result is different from that obtained previously [2] for the effect of adding alcohols or ethers on the photolysis of water over TiO_2 .

Figures 1 - 4 show the effects of the amount of alcohols or ethers added on the hydrogen yield. The numbers next to the points indicate the number of sequential illuminations to which the sample had been exposed. In some experiments hydrogen was the most abundant gaseous product. Shoulders at 1.5 min which were probably due to CH_4 for SiG + 0.4 ml ethyl ether and

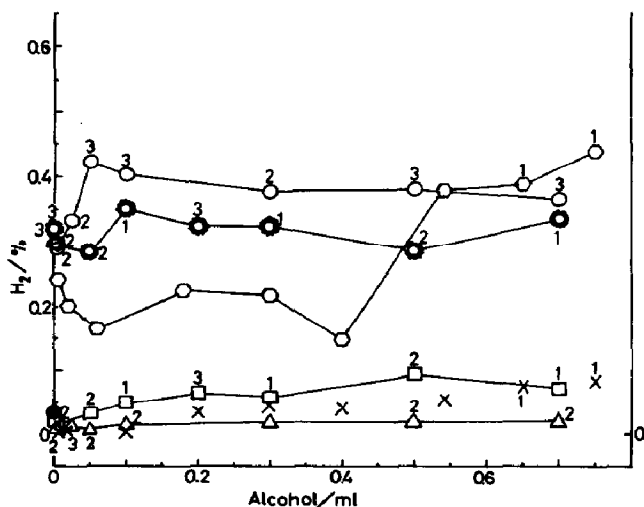


Fig. 1. The relation between the hydrogen yield and the amount of alcohol added: ●, 5.5 g SiG + 0.5 g $\text{Ti}(\text{OBu})_4$; ○, 5.5 g SiG + 0.5 g $\text{Ti}(\text{OBu})_4$ + methanol; ◐, 5.5 g SiG + 0.5 g $\text{Ti}(\text{OBu})_4$ + *n*-butanol; ◑, 5.5 g SiG + 0.5 g $\text{Ti}(\text{OBu})_4$ + isopropanol; △, 5.5 g SiG + methanol; ◒, 5.5 g SiG + *n*-butanol; ×, 5.5 g SiG + isopropanol.

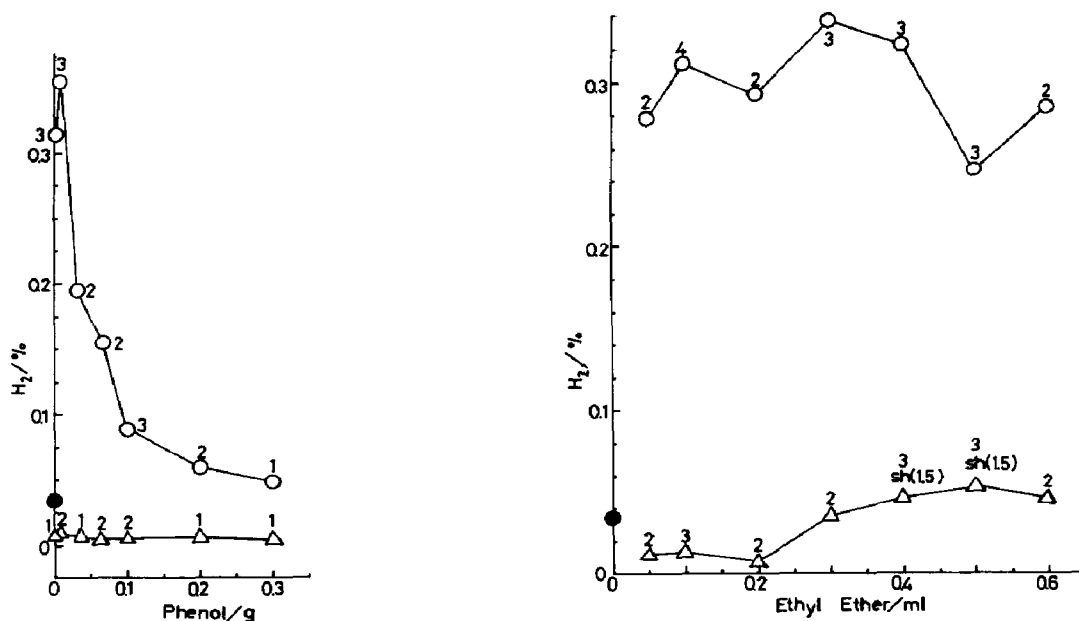


Fig. 2. The relation between the hydrogen yield and the amount of phenol added: ●, 5.5 g SiG + 0.5 g Ti(OBu)₄; ○, 5.5 g SiG + 0.5 g Ti(OBu)₄ + phenol; △, 5.5 g SiG + phenol.

Fig. 3. The relation between the hydrogen yield and the amount of ethyl ether added: ●, 5.5 g SiG + 0.5 g Ti(OBu)₄; ○, 5.5 g SiG + 0.5 g Ti(OBu)₄ + ethyl ether; △, 5.5 SiG + ethyl ether.

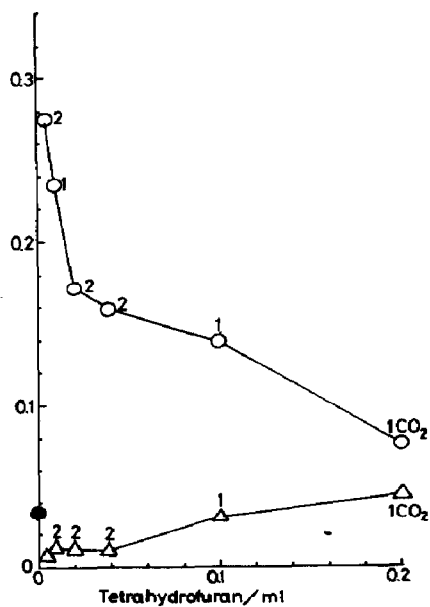


Fig. 4. The relation between the hydrogen yield and the amount of THF added: ●, 5.5 g SiG + 0.5 g Ti(OBu)₄; ○, 5.5 g SiG + 0.5 g Ti(OBu)₄ + THF; △, 5.5 SiG + THF.

SiG + 0.5 ml ethyl ether and CO₂ for SiG + Ti(OBu)₄ + 0.2 ml tetrahydrofuran (THF) and SiG + 0.2 ml THF were detected by gas-liquid chromatography using Porapak-Q (Figs. 3 and 4).

In Fig. 5 the change in the hydrogen concentration in the exit gas after illumination for 10 min is plotted against the number of illuminations for each catalyst treated with an alcohol or an ether. The intervals represented by full and broken lines are 15 min and 20 - 240 h respectively. Repeated illumination reduces the catalytic activity which recovers after 20 h as shown in Fig. 5.

In order to confirm that the hydrogen in the exit gas was generated from the decomposition of water, we performed the following two experiments.

(1) The sixteenth illumination using the catalyst SiG + Ti(OBu)₄ + 0.75 ml isopropanol, which is shown in Fig. 5, was performed in the presence of dry nitrogen. The hydrogen concentration in the exit gas was found to be 0.113 vol.%. The seventeenth illumination was performed with water-saturated nitrogen gas in the reaction tube and the hydrogen concentration in the exit gas increased to 0.947 vol.%. It is assumed that in the first case the hydrogen is formed from water adsorbed on the catalyst and in the second case it is formed from water in the carrier gas.

(2) The second experiment was performed using D₂O (purity, 100% D) instead of H₂O. In order to remove the adsorbed water dry nitrogen gas was passed through the reaction tube containing the catalyst SiG + Ti(OBu)₄ + 0.7 ml *n*-butanol for about 24 h prior to the first illumination. When no

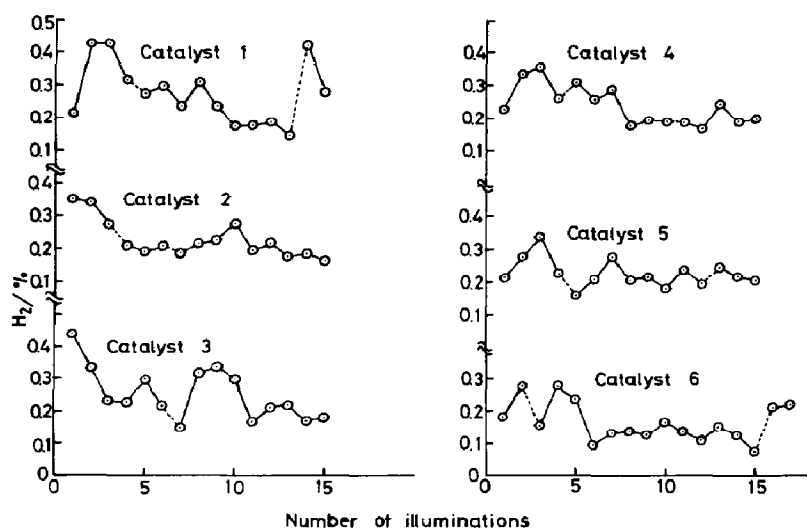
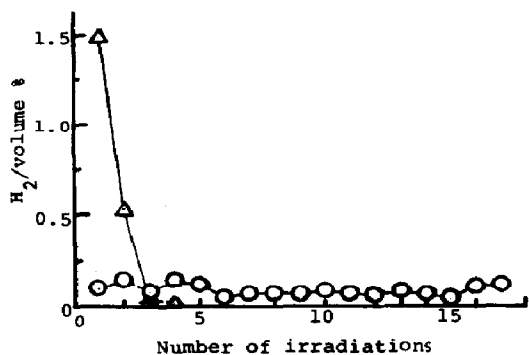
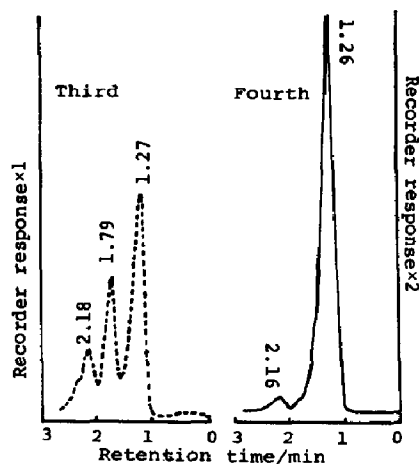


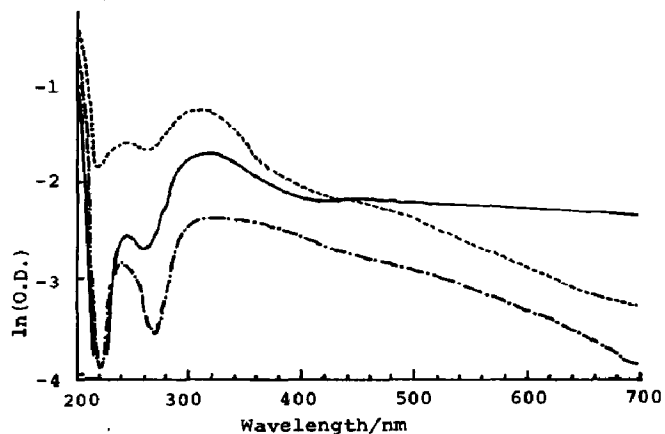
Fig. 5. Change in the hydrogen concentration in the exit gas: catalyst 1, 5.5 g SiG + 0.5 g Ti(OBu)₄ + 0.05 ml methanol; catalyst 2, 5.5 g SiG + 0.5 g Ti(OBu)₄ + 0.1 ml *n*-butanol; catalyst 3, 5.5 g SiG + 0.5 g Ti(OBu)₄ + 0.75 ml isopropanol; catalyst 4, 5.5 g SiG + 0.5 g Ti(OBu)₄ + 0.0080 g phenol; catalyst 5, 5.5 g SiG + 0.5 g Ti(OBu)₄ + 0.3 ml ethyl ether; catalyst 6, 5.5 SiG + 0.5 g Ti(OBu)₄ + 0.00488 ml THF.



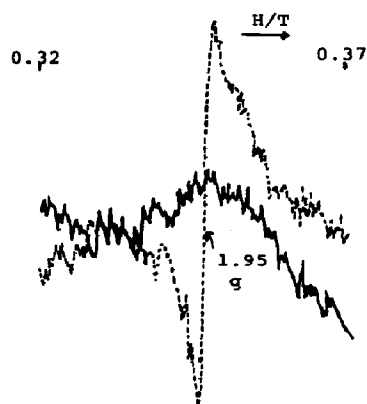
(a)



(b)



(c)



(d)

Fig. 6. Comparison of (a) the hydrogen concentrations in the exit gas, (b) the gas chromatograms, (c) the diffuse reflectance spectra and (d) the ESR spectra for catalysts treated with various amounts of THF: ○, —, 5.5 g SiG + 0.5 g Ti(OBu)₄ + 0.004 88 ml THF; Δ, — — —, 5.5 g SiG + 0.5 g Ti(OBu)₄ + about 20 ml THF; — · —, 5.5 g SiG + 0.004 88 ml THF.

hydrogen was detected in the exit gas, D₂O-saturated nitrogen was passed through the reaction tube for about 20 min. After illumination for 10 min the exit gas was analysed by mass spectrometry. Only D₂ was detected; no H₂ or DH was found within the limits of experimental error (0.002 mol.%).

The change in the hydrogen concentration in the exit gas after illumination for 10 min, the gas chromatogram obtained using Porapak-Q, the diffuse reflectance spectrum and the electron spin resonance (ESR) spectrum for the THF-treated catalyst are compared in Fig. 6 with the results obtained for a catalyst prepared by the addition of a large amount (about 20 ml) of THF.

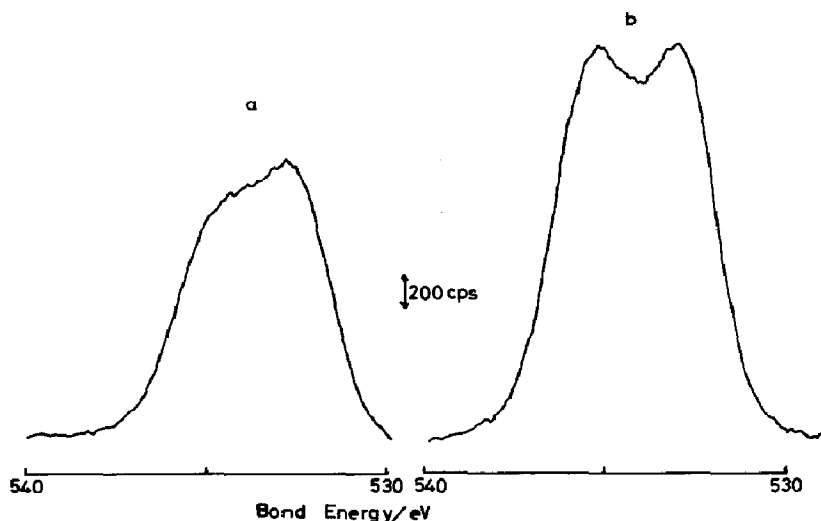
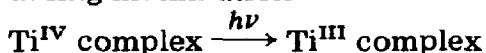
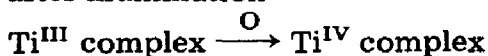


Fig. 7. The X-ray photoelectron spectra of O 1s for the catalyst 5.5 g SiG + 0.5 g Ti(OBu)₄ + 0.05 ml methanol: curve a, before illumination; curve b, after 15 illuminations.

A possible catalysis mechanism which may result in the continuous generation of hydrogen is as follows:
during illumination



after illumination



Some oxygen species were detected as O₃ and N₂O. Figure 7 shows the X-ray photoelectron spectra of O 1s for the catalyst SiG + Ti(OBu)₄ + 0.05 ml methanol before and after 15 consecutive illuminations (see Fig. 5). About 2 eV of the bond energy difference can be interpreted as being due to adsorbed oxygen or to effects caused by changes in the valence electrons of the oxygen atoms in the complex.

We are continuing the study of the electron states of the catalysts by measuring the electronic spectra, the ESR spectra, the X-ray photoelectron spectra, the IR spectra and the nuclear magnetic resonance spectra. We have obtained some data on the oxygen produced by the photolysis of water, although it is very difficult to measure the amount produced.

We wish to thank Dr. N. Wasada of the National Chemical Laboratory for Industry for measuring the mass spectra.

- 1 G.N. Schrauzer and T. D. Guth, *J. Am. Chem. Soc.*, **99** (1977) 7189.
H. van Damme and W. K. Hall, *J. Am. Chem. Soc.*, **101** (1979) 4373.
S. Sato and J. M. White, *Chem. Phys. Lett.*, **72** (1980) 83.
T. Kawai and T. Sakata, *Chem. Phys. Lett.*, **72** (1980) 87.
- 2 T. Sakata and T. Kawai, *Chem. Phys. Lett.*, **80** (1981) 341.
- 3 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley-Interscience, New York, 1972.