

THE OXIDIZING PRODUCTS OF THE PHOTOLYSIS OF WATER CATALYSED BY THE TITANIUM(IV) COMPLEX FORMED FROM POLYMERIZED *n*-BUTYL-*o*-TITANATE AND METHANOL

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Summary

The complex formed by direct reaction between polymerized *n*-butyl-*o*-titanate and methanol in a benzene solution catalyses the photocatalytic decomposition of water. In this paper the results of the photolysis of water over the catalyst together with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ or catalase are compared with the results of photolysis over the catalyst alone.

1. Introduction

The complex formed by direct reaction between polymerized *n*-butyl-*o*-titanate ($\text{Ti}(\text{O}i\text{Bu})_4(\text{pol})$) and methanol in a benzene solution is one of several catalysts which promote the photocatalytic decomposition of water [1]. Its structural formula has been suggested to be $\text{Ti}_7(\text{O}i\text{Bu})_{12}(\text{OMe})_4\text{O}_6$ on the basis of measurements of the ^1H and ^{13}C nuclear magnetic resonance spectra, the X-ray photoelectron spectra and the UV absorption spectra. $[\text{Ti}(\text{OMe})(\text{O}i\text{Bu})\text{O}_4]$ and $[\text{Ti}(\text{O}i\text{Bu})_2\text{O}_4]$ shown in Fig. 1 are the smallest clusters in the complex and $\text{Ti}(\text{O}i\text{Bu})_4(\text{pol})$ respectively. The complex consists of the local unit of only the latter cluster. The potential field around the titanium site in the $[\text{Ti}(\text{OMe})(\text{O}i\text{Bu})\text{O}_4]$ unit is disturbed asymmetrically compared with that of the $[\text{Ti}(\text{O}i\text{Bu})_2\text{O}_4]$ unit, which might induce a characteristic feature of the electronic state of the $[\text{Ti}(\text{OMe})(\text{O}i\text{Bu})\text{O}_4]$ unit in the complex, which is similar to that on the surface of TiO_2 , that may serve as a reference for the results of the quantitative calculations for TiO_2 [2]. However, the results of chromatographic analysis of the gas at the exit of the reaction tube indicate that the amount of the oxidizing products

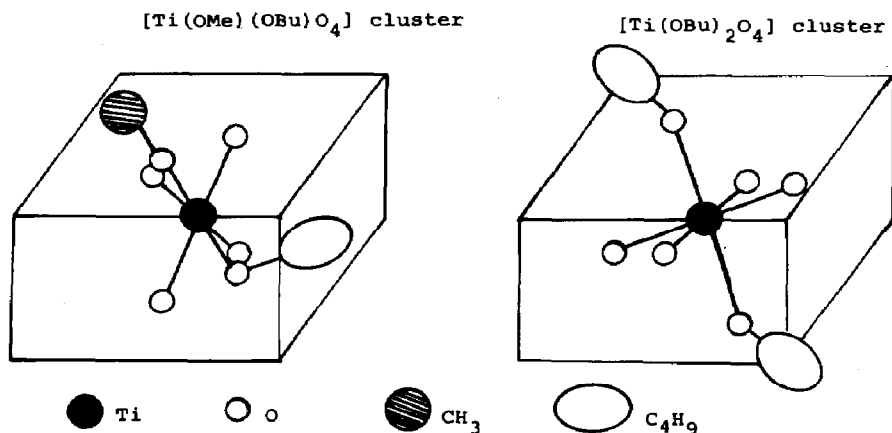


Fig. 1. Structures of the $[\text{Ti}(\text{OMe})(\text{OBu})\text{O}_4]$ and $[\text{Ti}(\text{OBu})_2\text{O}_4]$ clusters.

is less than that corresponding to $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$. The ratios of the O_3 and CO_2 yields to the hydrogen yield increased with repeated illumination as shown in Fig. 2. In a recent series of experiments we have found that the H_2O_2 product forms a complex with titanium(IV). The formation of H_2O_2 on the surface of TiO_2 powder during irradiation has been reported by Bickley and Vishwanathan [3]. In this paper the results of the photolysis of water over the catalyst together with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ or catalase are compared with the results of photolysis over the catalyst alone.

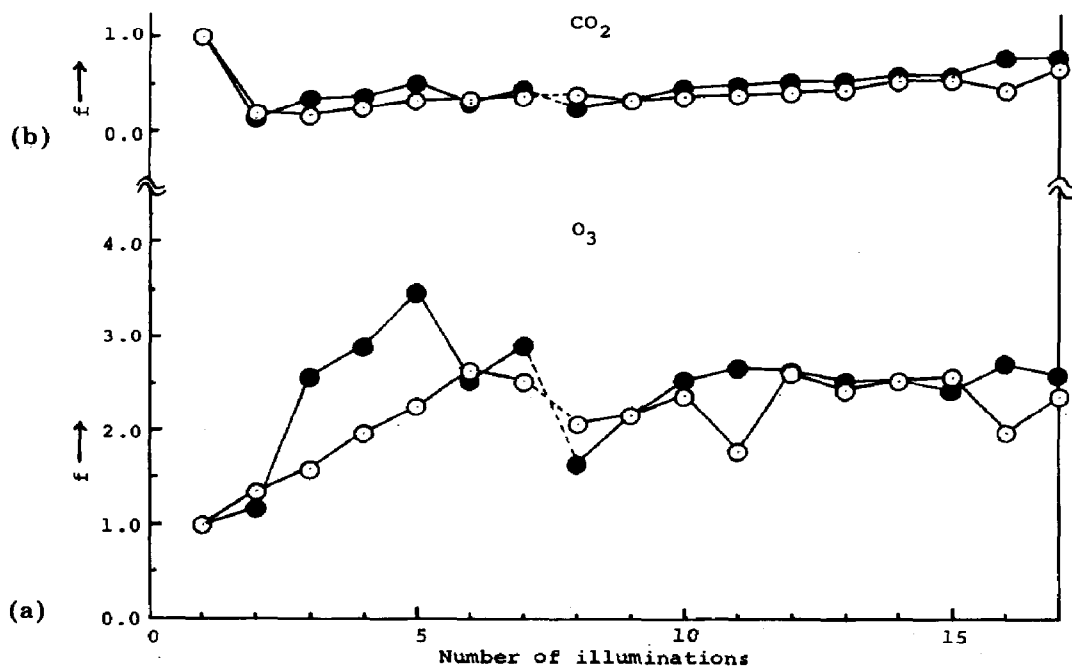


Fig. 2. Dependence of the ratio f of (a) the ozone yield and (b) the CO_2 yield to the hydrogen yield on the number of illuminations in the presence of catalysts 1 and 2 (catalyst 1 was prepared at room temperature and catalyst 2 was prepared in the refrigerator) (f is assumed to be unity at illumination 1): \circ , catalyst 1; \bullet , catalyst 2.

2. Experimental details

An alternative reaction apparatus to that used in previous work [1] was constructed to determine the minor reaction products. A cross-sectional diagram is shown in Fig. 3. A transparent quartz reaction tube with an external diameter of 20 mm was divided into an upper and a lower part by a quartz plate in which a large number of small holes about 0.5 mm in diameter had been punched. The catalyst was placed in the upper part. Water-saturated nitrogen gas at room temperature was passed through the reaction tube. The linear flow rate of nitrogen was the same as that in the previous measurement [1]. The gas at the exit of the reaction tube was analysed using Shimadzu 4A-PT and 4B-PT gas chromatographs together with a thermal conductivity detector under the following conditions: column dimensions, 3 mm \times 3 m and 3 mm \times 2 m; Porapak-Q and molecular sieve 5A; temperature, 50 $^{\circ}$ C and 80 $^{\circ}$ C; carrier gases, nitrogen and helium at flow rates of 80 ml min $^{-1}$ and 40 ml min $^{-1}$ respectively in order to increase the sensitivity of detection.

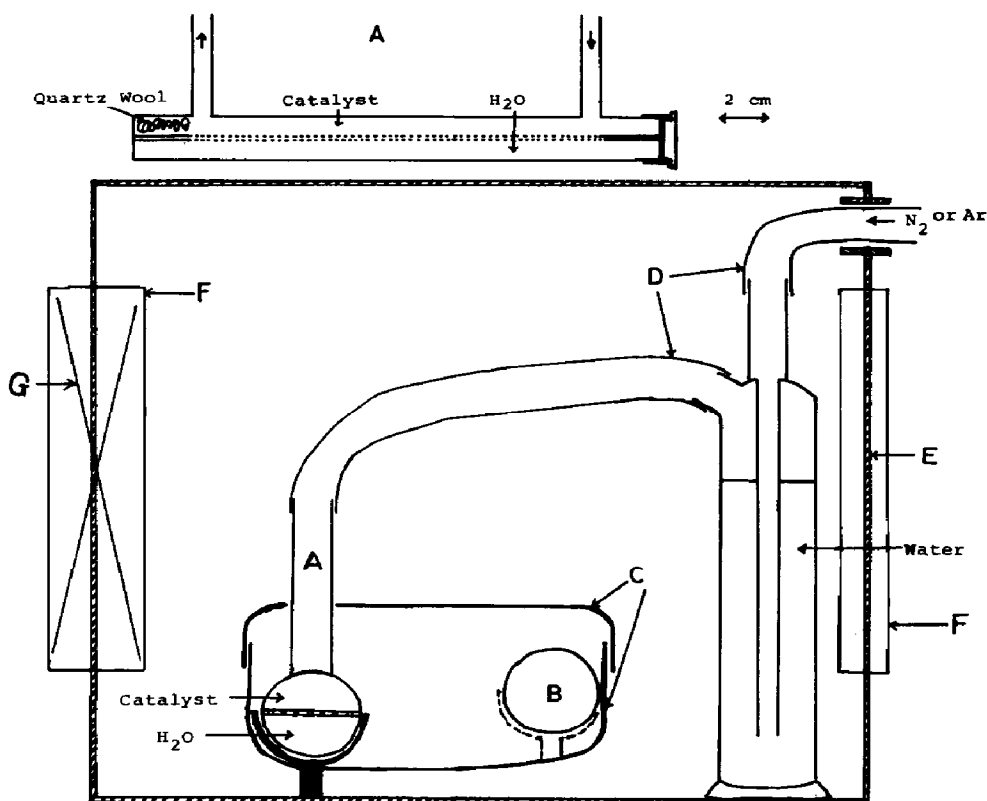


Fig. 3. Schematic diagram of the reaction apparatus: A, reaction tube; B, Toshiba H400-P mercury lamp; C, aluminium reflector; D, vinyl tube; E, casing; F, ventilating window; G, fan.

3. Results and discussion

Ozone (O_3) was the most abundant gaseous oxidizing product in all the experiments. The CO_2 yield was less than 5% of the H_2 yield. Another gaseous oxygen-containing product was identified as CH_3OH . There is no direct relation between the hydrogen yield and the CH_3OH yield. However, a small quantity of coloured catalyst was found after some illuminations. Although the colour is similar to that of the catalyst prepared by the addition of a large amount (about 20 ml) of tetrahydrofuran, which has been reported previously (see ref. 1, Fig. 6), its UV absorption spectrum in 60% $HClO_4$

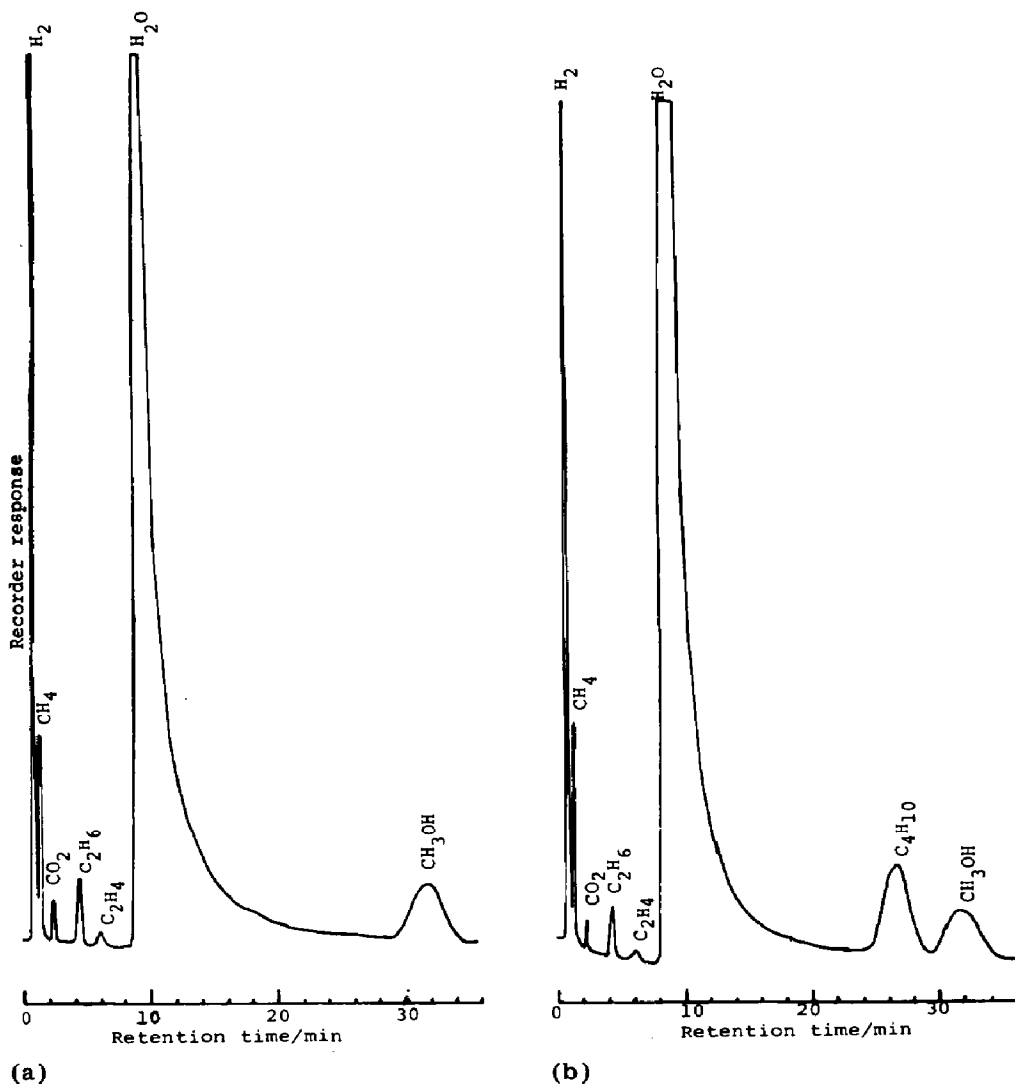


Fig. 4. Comparison of the gas chromatograms obtained using Porapak-Q after the second illumination: (a) catalyst only (8.25 g SiG + 0.75 g $Ti(OBu)_4$ + 0.075 ml methanol); (b) catalyst together with 8.25 g $FeSO_4 \cdot 7H_2O$.

showed no absorption band at 500 cm^{-1} which is attributed to the transition of the 3d electron of Ti^{3+} . Therefore the coloured catalyst is assumed to be a titanium(IV) complex. If H_2O_2 is produced during the illumination and forms a titanium(IV) complex with the catalyst, the same colour that is well known as an indicator of H_2O_2 in qualitative analysis [4] is observed.

We performed some experiments aimed at investigating this behaviour. The mercury lamp was moved nearer the reaction tube (the tube-lamp distance was about half that shown in Fig. 3) and the results of the photolysis of water over the catalyst (8.25 g silica gel (SiG) + 0.75 g $\text{Ti}(\text{OBU})_4$ + 0.075 ml methanol) together with 8.25 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were compared with those obtained over the catalyst alone. The catalyst was prepared in the same way as catalyst 1. The gas at the exit of the reaction tube was analysed after illumination for 5 min. Figure 4 shows the gas chromatograms obtained using Porapak-Q after the second illumination; the changes in the hydrogen, ozone, CO_2 , CH_4 and CH_3OH yields are plotted against the number of illuminations in Figs. 5 - 7. The following results were obtained when $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ was added to the catalyst: a new gaseous product (C_4H_{10}) was formed, the hydrogen yield was larger on the first day

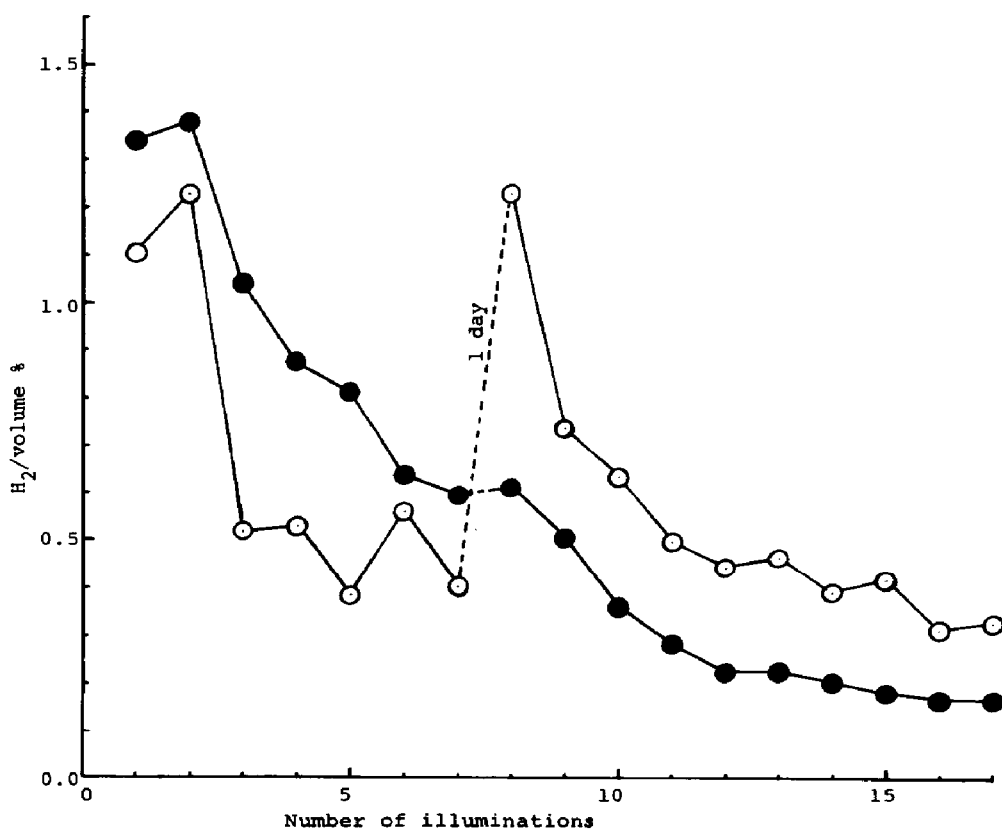


Fig. 5. Change in the hydrogen concentration in the exit gas: \circ , over 8.25 g SiG + 0.75 g $\text{Ti}(\text{OBU})_4$ + 0.075 ml methanol; \bullet , over 8.25 g SiG + 0.75 g $\text{Ti}(\text{OBU})_4$ + 0.075 ml methanol + 8.25 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

but smaller on the second day, and the ozone and CO₂ yields decreased. The factors of the total yields of hydrogen, ozone, CO₂, CH₄, CH₃OH, C₂H₆ and C₂H₄ after seven illuminations each lasting for 5 min on the first day were 1.413, 0.59, 0.63, 1.32, 1.10, 0.72 and 1.05 respectively in the presence of FeSO₄·7H₂O. The catalyst became an orange colour indicating the formation of a titanium(IV) complex with H₂O₂ because the reaction proceeds rapidly in the presence of H₂SO₄ [4]. The production of C₄H₁₀ is believed to be due to the ease with which butoxyl groups can dealkylate when a complex is formed between Ti(OBu)₄(pol) and H₂O₂. The hydrogen yield initi-

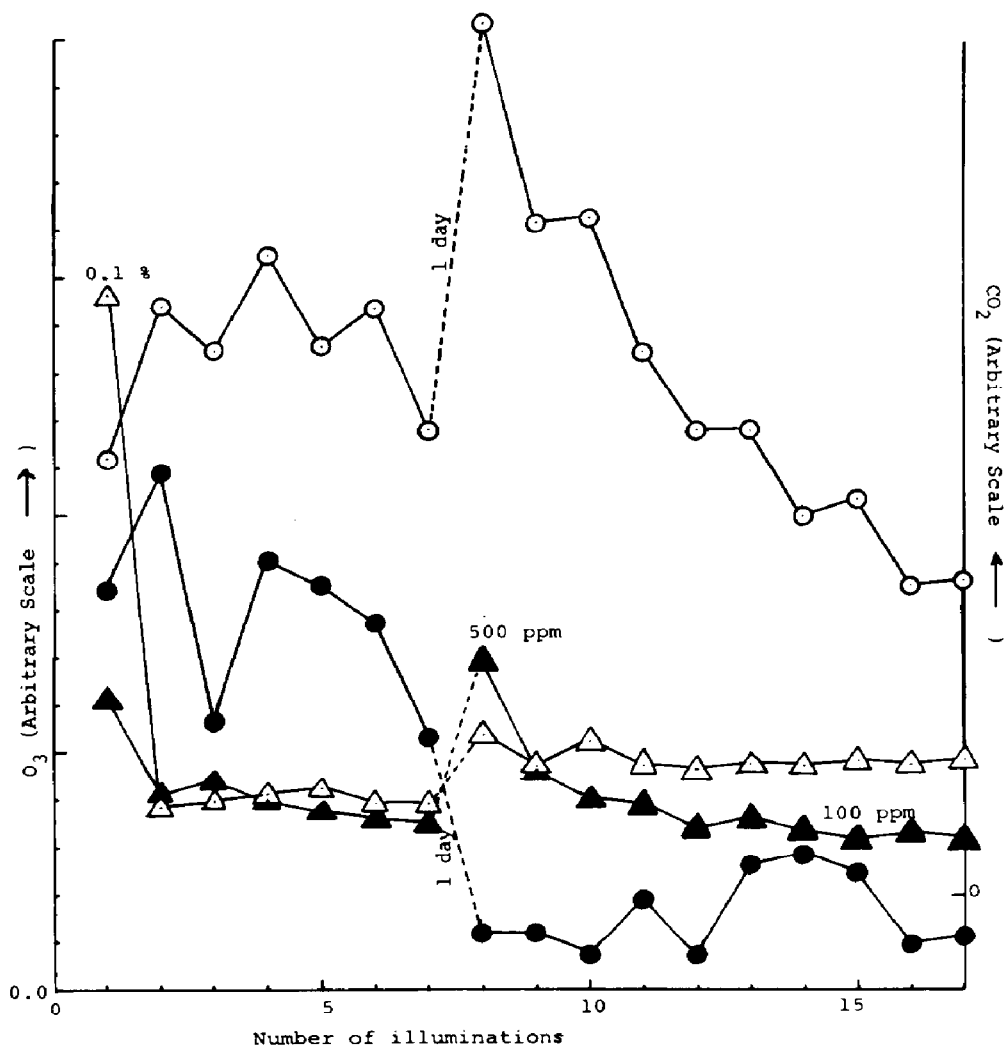


Fig. 6. Changes in the ozone and CO₂ yields: ○, ozone yield over 8.25 g SiG + 0.75 g Ti(OBu)₄ + 0.075 ml methanol; ●, ozone yield over 8.25 g SiG + 0.75 g Ti(OBu)₄ + 0.075 ml methanol + 8.25 g FeSO₄·7H₂O; △, CO₂ yield over 8.25 g SiG + 0.75 g Ti(OBu)₄ + 0.075 ml methanol; ▲, CO₂ yield over 8.25 g SiG + 0.75 g Ti(OBu)₄ + 0.075 ml methanol + 8.25 g FeSO₄·7H₂O.

ally increases owing to the reaction $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$. However, the activity of the catalyst decreases after 1 day. The decrease in the ozone and CO_2 yields may be due to the oxidation of Fe^{2+} .

The photolysis of water over the catalyst (5.5 g SiG + 0.5 g $\text{Ti}(\text{OBU})_4$ + 0.05 ml methanol) together with various quantities of catalase (P-L Biochemicals Inc.) was also investigated. The catalyst was prepared in the same way as catalyst 2 (or 2'). The changes in the hydrogen, ozone, CO_2 , CH_4 , C_2H_6 , C_2H_4 and CH_3OH contents in the exit gas after

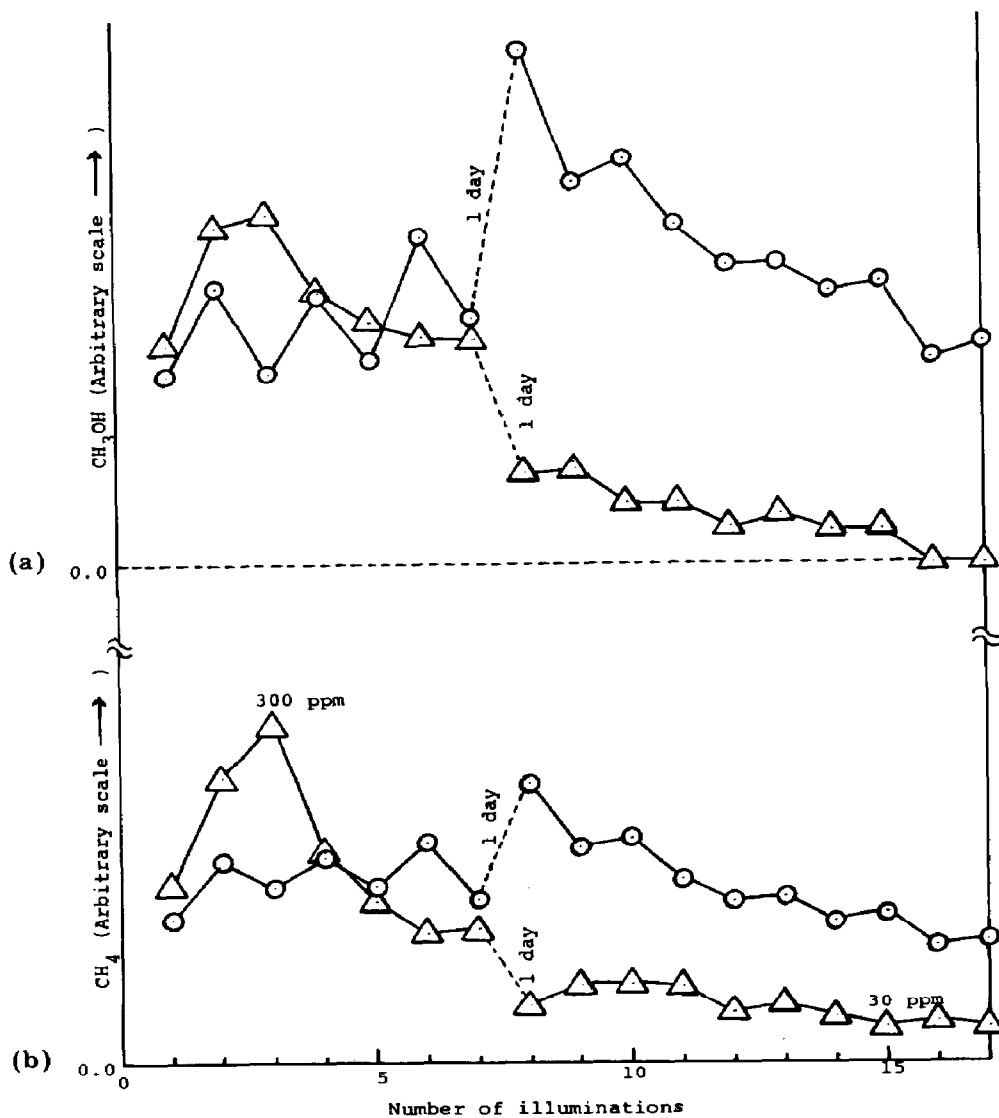


Fig. 7. Changes in (a) the CH_4 and (b) the CH_3OH yields: ○, over 8.25 g SiG + 0.75 g $\text{Ti}(\text{OBU})_4$ + 0.075 ml methanol; △, over 8.25 g SiG + 0.75 g $\text{Ti}(\text{OBU})_4$ + 0.075 ml methanol + 8.25 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

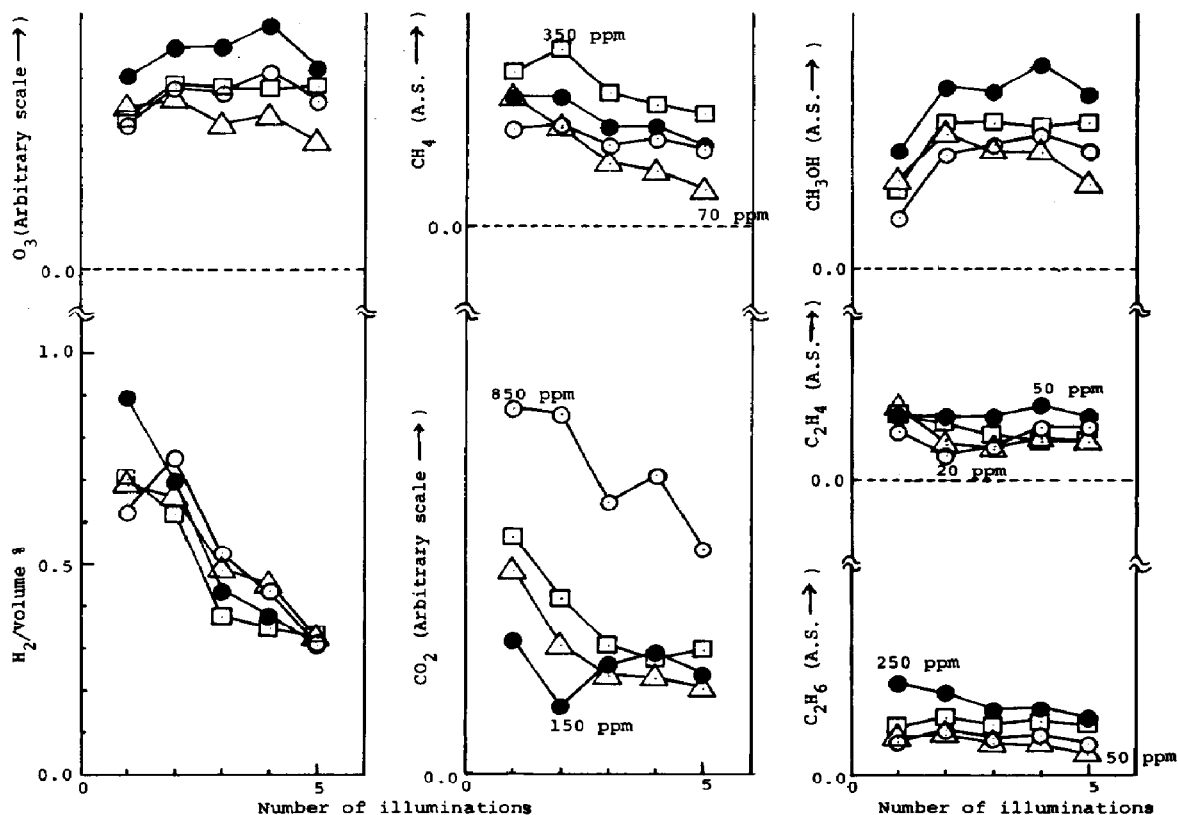
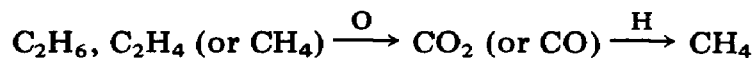
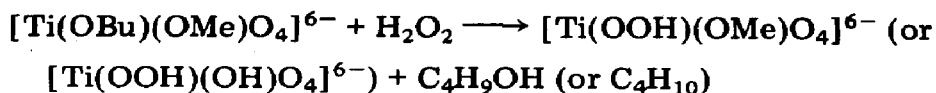
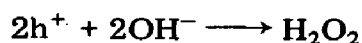


Fig. 8. Change in the hydrogen, ozone, CO₂, CH₄, C₂H₆, C₂H₄ and CH₃OH yields: ●, 5.5 g SiG + 0.5 g Ti(OBu)₄ + 0.05 ml methanol; ○, (5.5 g SiG + 0.5 g Ti(OBu)₄ + 0.05 ml methanol) + 2 ml catalase (absorbed in tissue paper); △, (5.5 g SiG + 0.5 g Ti(OBu)₄ + 0.05 ml methanol) + 1 ml catalase; □, (5.5 g SiG + 0.5 g Ti(OBu)₄ + 0.05 ml methanol) + (2.75 g SiG + 2 ml catalase).

illumination for 7 min are plotted against the number of illuminations for the catalyst plus catalase and for the catalyst alone in Fig. 8. The CO₂ and CH₄ yields increased and the hydrogen yield decreased in the presence of catalase which suggests that the reactions proceed as follows:



The colouring of the catalyst on illumination may be due to the following reaction sequence:



References

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