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Definition of the Intrinsic Rate of Photocatalytic Cleavage of Water over Pt–RuO_2/TiO_2 Catalysts

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The photocatalytic cleavage of water over Pt–RuO_2/TiO_2 catalysts under near UV illumination is investigated in a semicontinuous flow photoreactor. The effects of operational variables on the intrinsic rate of H_2 production, expressed per unit mass of catalyst per unit "transparency" of the reaction slurry, are investigated. It is shown that the intrinsic rate is a linear function of the intensity of incident illumination, an exponential function of the reaction temperature, and an exponential function of the steady-state pH value of the slurry. An equation describing the intrinsic rate of H_2 production over Pt–RuO_2/TiO_2 slurries is developed and values of the kinetic parameters are defined.

INTRODUCTION

The photocatalytic cleavage of water over semiconductor photocatalysts seems to be one of the most attractive means of converting solar into chemical energy (1–3). One of the most efficient semiconducting materials for this application is TiO_2 because of its high stability toward photocorrosion and its favorable band-gap energy and flat band potential. The evolution of H_2 by the cleavage of water is assisted by the presence of metal crystallites dispersed on the surface of TiO_2. After many investigations, the bifunctional photocatalytic system of Pt–RuO_2/TiO_2 has been found to be the most effective one for water splitting and H_2 production under UV irradiation (2, 4–7).

In previous studies in this laboratory (8, 9) the influence of various parameters related to the structure of the catalyst and various operating variables on the rate of H_2 production under UV illumination were investigated employing the Pt–RuO_2/TiO_2 catalyst. It was found that the rate of H_2 production is independent of the details of surface structure of Pt and is not sensitive to the surface area of the catalyst or to the method of preparation of the semiconductor. However, the efficiency of the photocatalytic process is significantly affected by the crystallographic structure of TiO_2, while the rate of H_2 production is strongly dependent on the pH of the suspension and is a linear function of the stirrer speed of the suspension, the slope of which depends on the catalyst loading. Finally, an expression for the intrinsic rate of H_2 production was also developed, which may provide a common denominator for comparison of the performance of different catalyst formulations.

The intrinsic rate of H_2 production, r_i, is expressed in the form of $r_m/(I/I_0)$, where r_m is the rate of H_2 production per unit mass of catalyst and I/I_0 is the "transparency" of the slurry, which is the ratio of the measured intensity of illumination at the reactor cell outlet over the intensity at the same point, at zero catalyst loading. Similar expressions employed in the literature (1–3, 10, 11) describing the "quantum yield" of a photocatalytic process include the number of photons absorbed by the catalyst. In the case of homogeneous systems where the photons are absorbed directly by the reacted molecules, the number of absorbed photons can be estimated by the difference between the photons entering and the photons exiting the photoreactor. However, in the case of heterogeneous systems, of the incident photons on the photoreactor, a part is scattered, a part is absorbed by the catalyst, producing or not a photocatalytic reaction, and a part is transmitted by the suspension. Thus, the number of photons absorbed by the catalyst particles, required for the expression of the quantum yield, cannot be easily estimated. On the other hand, the ratio I/I_0 incorporates all the above-mentioned processes, i.e., light scattering, light absorption, light transmission, and the influence of all operational variables. In this way, the intrinsic rate of H_2 production, based on the parameters I/I_0, is independent of reactor geometry and catalyst loading.

The literature of photocatalytic water cleavage over heterogeneous catalysts lacks an intrinsic kinetic model describing the sensitivity of the intrinsic rate on process variables such as temperature, pH of the suspension, and intensity of the incident illumination. Such a kinetic model is presented in the present investigation, employing the Pt–RuO_2/TiO_2 catalyst to investigate the dependence of the intrinsic rate of H_2 production on operational variables under UV irradiation. An equation describing the intrinsic

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rate of H_2 production as a function of the intensity of the incident illumination, reaction temperature, and pH of the slurry is developed, which may assist in unifying the literature in this field.

EXPERIMENTAL

The semiconductor employed as catalyst component in the present study is TiO_2 (Degussa P25), used as received. In a series of experiments, TiO_2 was also prepared by hydrolysis of titanium isopropoxide (9), resulting in the anatase form of TiO_2, and by sintering of commercial TiO_2 at 1173 K for 5 h, resulting in the rutile form of TiO_2. The catalyst employed was the bifunctional catalyst 0.5% Pt–1% RuO_2/TiO_2, prepared by the incipient wetness impregnation technique, as described in a previous paper (8).

The anatase/rutile content of the catalysts was determined by quantitative X-ray diffraction analysis using a Philips PW1840 instrument with Cu$K\alpha$ radiation.

Hydrogen production rates were determined using an experimental apparatus which consists of a quartz thermostated (double-wall) photoreactor, a 1000-W Xe lamp equipped with a water filter to remove infrared radiation, a regulated nitrogen supply system which functions as carrier gas of H_2 produced in the photoreactor, and an on-line gas chromatograph with a reporting integrator.

The photoreactor is a quartz cell with optically flat entry and exit windows. The cell is equipped with an inlet line terminating in a fritted glass section through which gases can be dispersed into the suspension. The water volume was invariably 45 ml and the gas-phase volume 150 ml. In all cases, the distance between the photoreactor and the light source was 45 cm. The experimental procedure involved adjustment of the pH of the solution to the desired level by addition of appropriate quantities of NaOH or HCl, addition of a preweighed amount of catalyst, and adjustment of the temperature of the slurry to the desired value, followed by N_2 purging for 1 h, under continuous stirring, so as to remove dissolved oxygen. After this procedure, the suspension was exposed to light under continuous stirring, while N_2 was dispersed into the solution through a glass frit. The cell outlet was connected to a gas chromatograph through a gas sampling valve. Samples were periodically analyzed and the N_2 flow was continuously monitored. The pH and the temperature of the suspension were continuously monitored during the photolysis experiments. Several reproducibility tests were performed under various conditions. In all cases, the uncertainty in the measurements of H_2 production rates was found to be less than 5%. Furthermore, the operation of the photoreactor was tested periodically using a standard catalyst under standard conditions. Further details of the experimental setup and procedure have been reported elsewhere (8, 9).

The intensity of illumination, expressed in quanta per second, was measured by a photometric method, employing $K_3Fe(C_2O_4)_3$ as a chemical actinometer, according to a procedure which has been described previously (12). The intensity of illumination was varied by adjusting the outlet power of the lamp, within limits.

Photoconductivity measurements were carried out employing an instrument for current measurement (Keithley 617), a power supply, a thermocontrolled chamber, and a 100-W halogen lamp whose output is at wavelengths above 300 nm. For these measurements, the samples, which were in powder form, were formulated into pellets employing a hydraulic press, and an ohmic contact was obtained by sublimation of In wire.

RESULTS AND DISCUSSION

1. *Dependence of Intrinsic Rate of H_2 Production on the Intensity of Illumination*

The dependence of H_2 production rate on the intensity of illumination in the near UV region was investigated using a 1000-W Xe lamp whose outlet power could be varied within limits. H_2 production rates over the 0.5% Pt–1% RuO_2/TiO_2 catalyst, at various catalyst loadings between 4.5 and 80 mg, were determined in a thermostated reactor cell at 298 K and pH of 13, as a function of the intensity of illumination. The results presented in Fig. 1 indicate a linear relationship between the rate of H_2 production, r, and the intensity of the incident illumination, P, within the stated range of wavelengths (300–400 nm). The slope of the linear relationship seems to be a function of catalyst loading. Furthermore, when the value of incident photon flux is zero, the rate of H_2 production is

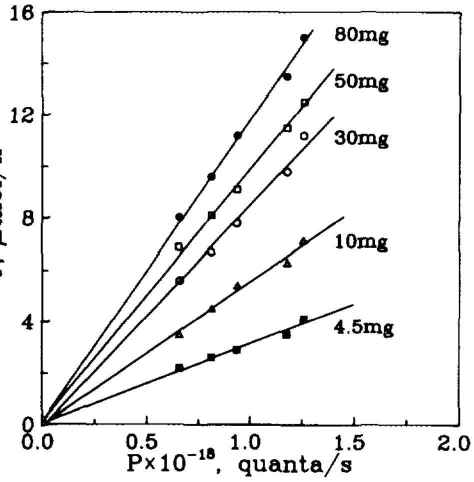

FIG. 1. Influence of the intensity of the incident illumination in the near UV region on the rate of H_2 production for different catalyst loadings at a pH of 13 and T = 298 K.

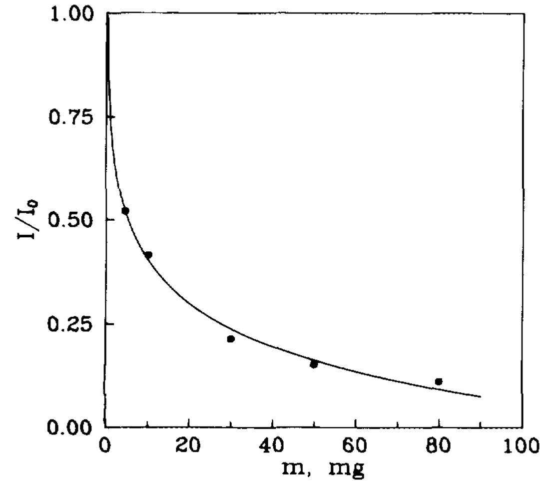

FIG. 2. Normalized intensity at the photoreactor cell outlet as a function of catalyst loading at a pH of 13 and T = 298 K.

also zero, as would be expected. The linear relationship between H_2 production rate and light intensity, if there is always sufficient catalyst loading with respect to the impinging photons, or, otherwise, the number of photons emitted within the same range of frequencies, is attributed to the proportionality between the number of photons absorbed by the catalyst and the number of electrons excited in the TiO_2 particles, which, in turn, is proportional to the number of H_2 molecules produced. Further details of this behavior have been discussed elsewhere (8).

The transparency of the reaction slurry, I/I_0, which was measured by an actinometric method (12), as a function of catalyst loading, is presented in Fig. 2. The curve of I/I_0 as a function of catalyst loading was determined under many different intensities of illumination and it was found to be constant, independent of the intensity of illumination. The intrinsic rate of H_2 production, $r_i = r_m/(I/I_0)$, computed on the basis of the values of the observed rate of H_2 production, the mass of catalyst employed, and the respective transparency, is illustrated in Fig. 3 as a function of the intensity of the incident illumination. The values of r_i, referred to the same value of P, correspond to different values of catalyst loading. It is evident that all the experimental points define the same straight line, which also passes through the origin, indicating that under otherwise identical conditions the intrinsic rate of H_2 production is only a function of the intensity of illumination in the near UV region. Thus, the intrinsic rate of hydrogen production as a function of the intensity of the incident illumination can be written as

$$r_i = \frac{r}{m(I/I_0)} = k_1 \cdot P. \qquad [1]$$

The reaction rate constant, k_1, depends on operational variables such as stirrer speed, pH, and reaction temperature. Under the experimental conditions pertaining to the results shown in Fig. 1, k_1 is estimated from Fig. 3 to be equal to 3.16×10^{-22} μmol/mg quantum at the reaction temperature of 298 K and pH of the slurry of 13.

2. *Influence of Reaction Temperature on the Intrinsic Rate of H_2 Production*

The influence of reaction temperature on the rate of H_2 production was investigated in the temperature region between 293 and 353 K. The results are presented in Fig. 4 in the form of Arrhenius plots for three values of catalyst loading (Fig. 4a) at pH of 13 and two values of pH (Fig. 4b) employing 45 mg of catalyst. An activation energy is observed in all cases, the value of which is 21 ± 2 kJ/mol. It is apparent from Fig. 4 that the activation energy is independent of the catalyst loading and the pH of the slurry. Using the values of the catalyst loading, m, and the respective values of I/I_0, the intrinsic rate of H_2 production can be calculated and the Arrhenius plots of Fig. 4 are transformed to those shown in Fig. 5. Thus, the intrinsic rate can be expressed as a function of temperature in the form

$$r_i = k_2 \cdot e^{-E/RT}, \qquad [2]$$

where E represents the activation energy of reaction, equal to 21 ± 2 kJ/mol, and k_2 is the pre-exponential factor, the value of which depends on the pH of the slurry. Based on the results of Fig. 5, k_2 assumes the value of 5800 μmol/h mg at pH of 13 and the value of 930 μmol/h mg at pH of 1.5, for constant intensity of illumination ($P = 1.18 \times 10^{18}$ quanta/s). The value of the activation energy of the reaction was found to be independent of the intensity of the incident illumination, which was varied

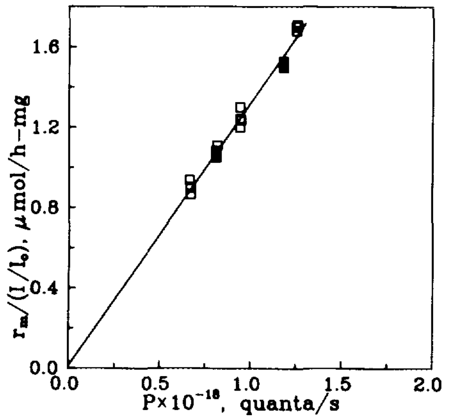

FIG. 3. Intrinsic rate of H_2 production as a function of the intensity of the incident illumination in the near UV region at a pH of 13 and T = 298 K.

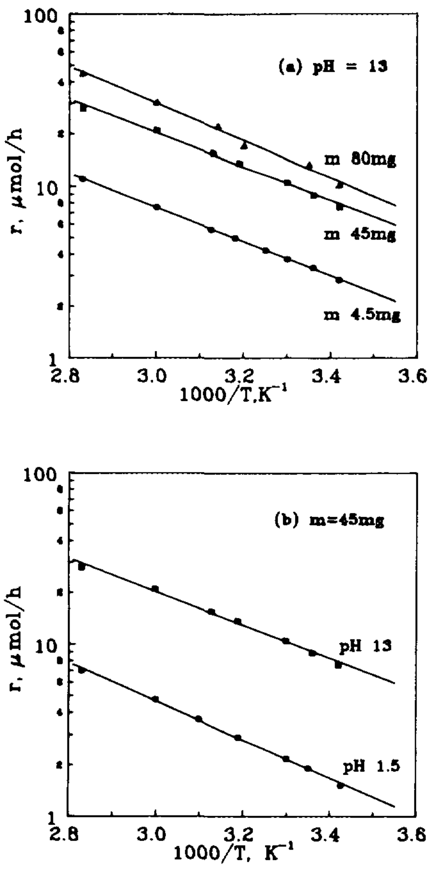

FIG. 4. Influence of temperature of the suspension on the rate of H_2 production at (a) various catalyst loadings at pH of 13 and (b) various pH values. The intensity of the incident illumination is 1.18 × 10^{18} quanta/s in all cases.

between 0.7 × 10^{18} and 1.3 × 10^{18} quanta/s in the near UV region.

The existence of an activation energy barrier for the photocatalytic cleavage of water over TiO_2-based catalysts has also been reported by other investigators (13, 14) and has mainly been linked with the increase of desorption of adsorbed products (H_2 and/or O_2) with increasing temperature (13) or with the reduction of the O_2 concentration in the solution with increasing temperature (14). However, neither of these reasons can adequately explain experimental observations. The former explanation would be reasonable if the rate-controlling step of the entire photocatalytic water cleavage process was the desorption of H_2. However, it has been demonstrated earlier (8) that H_2 desorption is not a slow step in the photocatalytic cycle. In order to further investigate this possibility, the activation energy was determined for small (4 Å) and large (18 Å) Pt particles dispersed on TiO_2 and no difference in its value was observed, indicating that H_2 desorption is not responsible for the existence of activation energy. On the other hand, the reduction of the concentration of oxygen in the solution with increasing temperature cannot be responsible for the observed activation energy, since, in the present experimental procedure, N_2 gas was continuously flowing through the suspension maintaining the oxygen concentration at very low levels.

To provide an explanation for the existence of the activation energy, the variation of the rate of H_2 production with reaction temperature was also investigated separately for an anatase and a rutile TiO_2 catalyst sample. The results, illustrated in Fig. 6, indicate that the value of the activation energy of the photocatalytic reaction depends on the crystallographic structure of TiO_2. The activation energy is found to be 27 kJ/mol (or 0.3 eV) for the anatase form of TiO_2 and 18.5 kJ/mol (or 0.2 eV) for

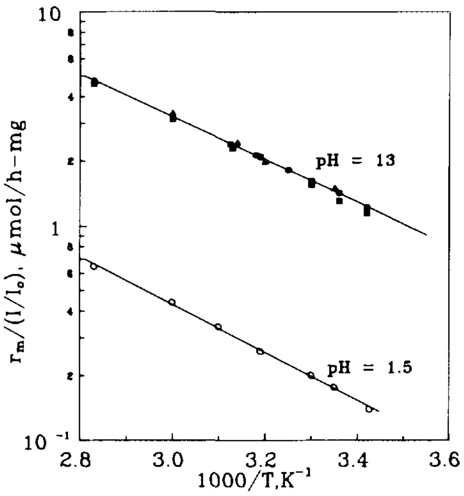

FIG. 5. Intrinsic rate of H_2 production as a function of reaction temperature.

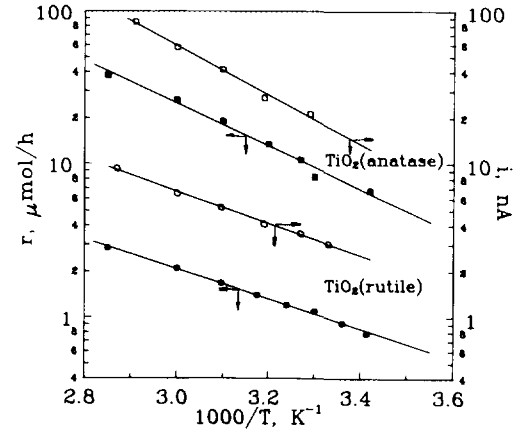

FIG. 6. Influence of temperature on (left axis) the rate of H_2 production and (right axis) the photocurrent for different structural forms of TiO_2.

the rutile form of TiO_2. The value of 21 kJ/mol reported earlier (Fig. 4) corresponds to the commercial TiO_2 (Degussa P25), which is composed of 80% anatase and 20% rutile. The enhanced photocatalytic efficiency of the anatase form of TiO_2 is attributed to its cathodically shifted flat band potential with respect to that of rutile, as has already been discussed elsewhere (9, 15). In order to explain the observed difference in the value of the activation energy of the photocatalytic reaction for the two different forms of TiO_2, the variation of the photocurrent, i, with temperature was also investigated for the two crystallographic forms of TiO_2 and the results are also illustrated in Fig. 6 in the form of plots of log photocurrent versus reciprocal temperature. It is apparent that the photocurrent depends exponentially on reciprocal temperature, giving rise, as it were, to an "activation energy" of photoconductivity. The values of the "activation energy" of photoconductivity are estimated from the plots of Fig. 6 and found to be approximately 0.3 eV for the anatase form of TiO_2 and approximately 0.2 eV for the rutile form of TiO_2. These values are identical to those of the activation energy of the photocatalytic process. Based on these results, it may be concluded that the observed activation energy barrier of the photocatalytic water cleavage over the present catalysts is due to the variation of photoconductivity of TiO_2 with temperature. The reason for the existence of this temperature dependence of photoconductivity may be the existence of deep traps in the forbidden band of TiO_2 (16–19) or a Fermi level shift caused by variation of temperature (13b).

Regardless of the exact mechanism giving rise to the existence of activation energy of photoconductivity, enhancement of photoconductivity implies increase of the concentration and mobility of electron–hole pairs in the bulk of TiO_2, which are the charge-carrier species. The increase of electrons in the conduction band of TiO_2 results in an increase of H_2 production rate according to

$$2H_2O + 2e^-(TiO_2) \xrightarrow{Pt} H_2 + 2OH^-. \qquad [3]$$

3. *Dependence of the Intrinsic Rate of H_2 Production on pH*

The influence of the pH of the suspension on the rate of H_2 production has been investigated and discussed elsewhere (8, 20). It was demonstrated in those studies that the rate of H_2 production is strongly dependent on the pH of the suspension. As pH increases, the rate also increases and the enhancement of the rate with increasing pH becomes more pronounced when the pH exceeds 10. This behavior has been attributed (8, 20) to the increased concentration of physisorbed OH^- groups at higher pH values which participate in the electorn–hole separation process, intervening in O_2 uptake by the TiO_2 particles and hole scavenging to produce O^- or oxygen. It was also observed that during the course of the reaction the pH of the suspension varied with time (8). This investigation was completed by the simultaneous measurement of the variation of the rate of H_2 production and the value of pH of the suspension with time of reaction, over the entire pH scale. The variation of the rate and pH of the suspension with time is illustrated in Fig. 7 for four different catalyst loadings. In all cases, the initial pH of the solution was adjusted to 10. It is obvious that the variation of the rate of H_2 production follows very closely the variation of the pH of the slurry with time. It is also observed that both the steady rate and the steady pH of the suspension (after about 8 h of illumination) are functions of catalyst loading. Similar experiments of the simultaneous measurement of the variation of the H_2 production rate and the pH of the slurry with time of illumination were also conducted over the entire pH scale (1–14). In all cases, a difference in the value of pH of the suspension after about 8 h of illumination as compared to the initially adjusted pH value was observed. To estimate the intrinsic rate of H_2 production, the "transparency" of the reaction slurry, I/I_0, was also measured as a function of the pH of the suspension.

The influence of pH (final, steady-state value) on the intrinsic rate of H_2 production is illustrated in Fig. 8. It is

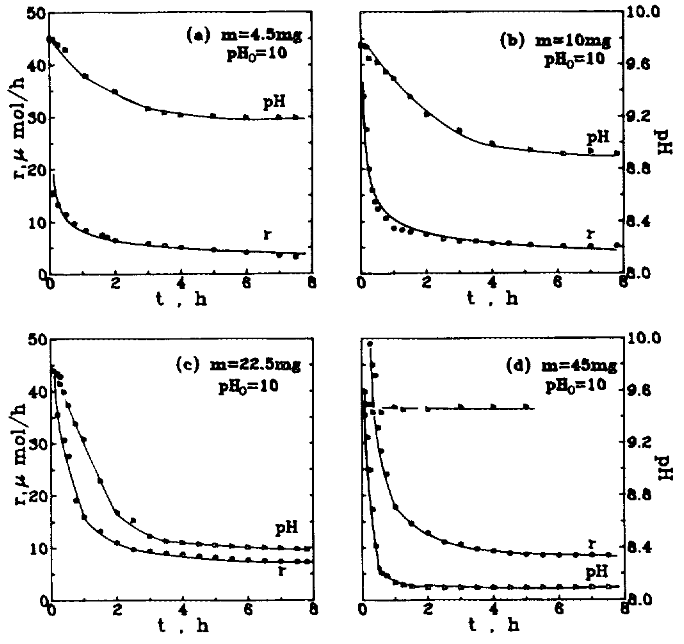

FIG. 7. Variation of the rate of H_2 production and pH of the slurry with time of irradiation for four different catalyst loadings and initially adjusted pH of 10. The variation of the pH for unmetallized TiO_2 (□) is also presented in (d).

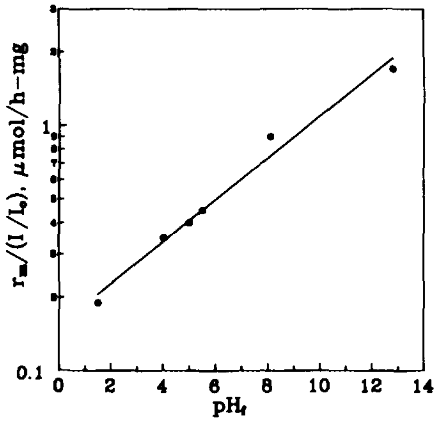

FIG. 8. Intrinsic rate of H_2 production as a function of the steady pH under illumination at $T = 298$ K and $P = 1.18 \times 10^{18}$ quanta/s.

observed that the intrinsic rate of H_2 production depends exponentially on the pH of the slurry. Following the results of Fig. 8, the intrinsic rate of H_2 production can be expressed as a function of pH in the form

$$r_i = k_3 \cdot e^{\alpha \mathrm{pH}} \qquad [4]$$

where α is a constant, equal to 0.19 ± 0.01, and k_3 is the pre-exponential factor, equal to 0.16 ± 0.05 μmol/h mg at constant temperature (298 K) and intensity of illumination (1.18×10^{18} quanta/s). The value of α was found to be independent of reaction temperature and intensity of the incident illumination.

4. *Intrinsic Rate of H_2 Production over the 0.5% Pt–1% RuO_2/TiO_2 Photocatalyst*

From the results presented in previous sections it is apparent that the intrinsic rate of H_2 production over the 0.5% Pt–1% RuO_2/TiO_2 catalysts, illuminated by near UV irradiation, can be defined as the observed rate of H_2 production per unit mass of catalyst, normalized with respect to the transparency of the slurry of the photoreactor. The intrinsic rate was found to be linearly dependent on the intensity of the incident illumination, P, exponentially dependent on the pH of the suspension and on reciprocal temperature. Mathematically, the intrinsic rate can be expressed as

$$\begin{aligned} r_i &= K_p \cdot K_{\mathrm{pH}} \cdot K_T \\ &= k_p P \cdot k_{\mathrm{pH}} e^{\alpha \mathrm{pH}} \cdot k_T e^{-E/RT} \\ &= k_0 e^{\alpha \mathrm{pH}} e^{-E/RT} P, \end{aligned} \qquad [5]$$

where k_0, α, and E are constants. The value of α was found to be equal to 0.19, while the value of the activation energy, E, was found to be equal to 27 kJ/mol when anatase TiO_2 is used, 18.5 kJ/mol when rutile TiO_2 is used, and 21 kJ/mol when commercial TiO_2 (80% anatase, 20% rutile) is used. The value of the constant k_0 can be obtained from the variation of the intrinsic rate with the intensity of the incident illumination (Fig. 3), from the variation of the intrinsic rate with temperature (Fig. 5), or from the variation of the intrinsic rate with the pH of the suspension (Fig. 8). Values of k_0 were thus estimated and are shown in Table 1. In all cases the values of k_0 are very close and a mean value of 1.6×10^{-19} μmol/mg quantum can be estimated. The constancy of the value of k_0 over widely different experimental conditions, as shown in Table 1, may also indicate that the only parameters which affect the intrinsic rate of H_2 production are those which have been accounted for and that no other important parameters have been erroneously omitted.

It was shown in a previous publication (8) that the rate of H_2 production is a weak function of the speed of the stirrer which is employed to maintain the slurry in suspension. This phenomenon is related to the frequency by which the individual catalyst particles are illuminated as they pass in front of the cell window through which light is introduced. Thus, the stirrer speed can influence the value of k_0. This influence cannot be easily quantified and generalized since the particle distribution inside the photoreactor cell is not known and it depends strongly on the geometry of the cell. It was also shown, however, that under certain experimental conditions (high stirrer speed and low catalyst loading) the influence of stirring speed on the observed rate is minimal or nonexistent. Thus, experiments conducted to determine the intrinsic rate of H_2 production in photocatalytic cells should be conducted under such conditions.

TABLE 1

Values of k_0 Estimated from the Experimental Results Following Eq. [5]

P ($\times 10^{-18}$ quanta/sec)	pH	T (K)	k_0 ($\times 10^{19}$ μmol/mg quantum)
0.67–1.25	13	298	1.55
0.67–1.25	13	313	1.50
0.67–1.25	13	323	1.62
0.67–1.25	1.5	298	1.75
0.67	13	298–323	1.50
1.18	13	298–323	1.30
1.18	1.5	298–323	1.65
1.25	13	298–323	1.48
1.18	1.5–13	298	1.75
1.18	1.5–13	313	1.80
1.18	1.5–13	323	1.66
0.67	1.5–13	298	1.57

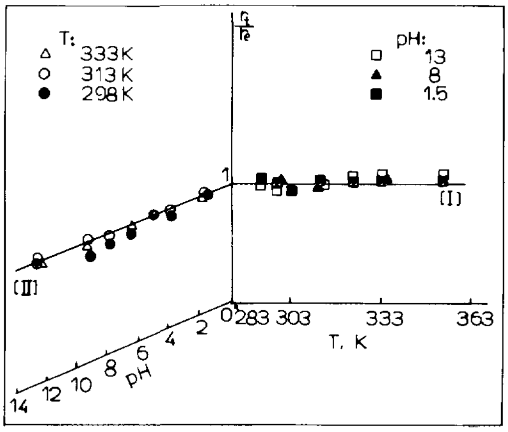

FIG. 9. Comparison of theoretical and experimental values of the intrinsic rate of H_2 production at selected values of pH and temperature.

It was also found that the rate of H_2 production is slightly dependent on RuO_2 loading, presenting a maximum at 1% RuO_2 and is nearly independent of Pt loading, at loadings above 1% Pt, while a weak maximum is observed at 0.5% Pt (8). Thus, it can be concluded that Eq. [5] describes very closely the intrinsic rate of H_2 production, independent of RuO_2 or Pt loadings. The term which is slightly affected by RuO_2 or Pt loading is k_0, while the values of α and E are independent of these parameters.

An integral test (one in which all parameters are simultaneously accounted for) of the validity of the derived kinetic expression (Eq. [5]) with the stated values of the kinetic parameters is provided in Fig. 9. In this figure, the ratio of the theoretical value of the intrinsic rate (r_t), as obtained by Eq. [5], over the value of the intrinsic rate as obtained experimentally (r_e) is presented as a function of temperature and pH of the suspension. All combinations of temperature and pH ideally ought to define a plane, parallel to the T–pH plane, intersecting that r_t/r_e axis at the value of unity. In order to avoid the complications of three-dimensional plots, the data presented in Fig. 9 are either at constant pH (pH = 1.5, 8, and 13) or constant temperature (T = 298, 313, and 333 K). Thus, two ideal lines are defined, lines I and II in Fig. 9, onto which, ideally, the experimental points should fall. The distance of the experimental points from the ideal lines I and II indicates the magnitude of deviation of the experimental values of the intrinsic rate from the corresponding theoretical values, predicted by Eq. [5]. Figure 9 indicates that the experimental and theoretical values of the intrinsic rate almost coincide indicating that, within the range of parameter values employed in the present study, Eq. [5] is a good presentation of the intrinsic rate of H_2 production over $Pt–RuO_2/TiO_2$ photocatalysts.

CONCLUSIONS

The intrinsic rate, r_i, of the photocatalytic cleavage of water over $Pt–RuO_2/TiO_2$ slurries can be satisfactorily expressed by the relationship

$$r_i = \frac{r}{m\left(\frac{I}{I_0}\right)} = k_0 e^{a\mathrm{pH}} \cdot e^{-E/RT} P, \qquad [6]$$

where r is the observed rate of H_2 production, m is the catalyst loading, I/I_0 is the transparency of the slurry, a is the pre-exponential factor of the dependence of the rate on the pH of the slurry under illumination (~0.19), E is the activation energy of the reaction (~21 kJ/mol), P is the intensity of the incident irradiation in the near UV region, and k_0 is the rate constant (1.6×10^{-19} μmol/mg quantum).

The parameters a and E are independent of pH of the slurry, temperature, intensity of incident illumination, and Pt or RuO_2 loading of the catalysts. The value of the rate constant is also independent of pH, T, and P, but it is a weak function of Pt and RuO_2 loading of the catalysts.

REFERENCES

1. Harriman, A., and West, M. A., "Photogeneration of Hydrogen." Academic Press, New York, 1982.
2. Grätzel, M., Ed., "Energy Resources through Photochemistry and Catalysis." Academic Press, New York, 1983.
3. Serpone, N., and Pelizzetti, E. Eds., "Photocatalysis, Fundamentals and Applications." Wiley, New York, 1989.
4. Duonghong, D., Borgarello, E., and Grätzel, M., *J. Am. Chem. Soc.* **103,** 4685 (1981).
5. Kawai, T., and Sakata, T., *Nature* **286,** 474 (1980).
6. Blondeel, G., Harriman, A., and Williams, D., *Sol. Energy Mater.* **9,** 217 (1983).
7. Escudero, J. C., Cervera-March, S., Giménez, J., and Simarro, R., *J. Catal.* **123,** 319 (1990).
8. Karakitsou, K. E., and Verykios, X. E., *J. Catal.* **134,** 629 (1992).
9. Karakitsou, K. E., and Verykios, X. E., *J. Phys. Chem.* **97,** 1184 (1993).
10. Formenti, M., Juillet, F., Mériaudeau, P., and Teichner, S. J., *Chem. Technol.* **1,** 680 (1971).
11. (a) Augugliaro, V., Palmisano, L., and Schiavello, M., *AIChE J.* **37,** 1096 (1991); (b) Schiavello, M., Augugliaro, V., and Palmisano, L., *J. Catal.* **127,** 332 (1991).
12. Calvert, J. G., and Pitts, J. N., Eds. "Photochemistry." Wiley, New York, 1967.
13. (a) Pichat, P. and Herrmann, J. M., *in* "Photocatalysis, Fundamentals and Applications" (N. Serpone and E. Pelizzetti, Eds.). Wiley, New York, 1989. (b) Al-Ekabi, H. and Serpone, N., in "Photocatalysis, Fundamentals and Applications," (Serpone, N. and Pelizzetti, E. eds.), Wiley, New York 1989.
14. Borgarello, E., Kiwi, J., Pelizzetti, E., Visca, M., and Grätzel, M., *J. Am. Chem. Soc.* **103,** 6324 (1981).

15. Rao, M. V., Rajeshwar, K., Pal. Vernerker, V. R., and Dubow, J., *J. Phys. Chem.* **84,** 1987 (1980).
16. Chosh, A. K., Wakim, F. G., and Addiss, J. R. R., *Phys. Rev.* **184,** 979 (1969).
17. Chosh, A. K., Lauer, R. B., and Addiss, J. R. R., *Phys. Rev. B* **8,** 4842 (1973).
18. Kingsbury, R. J., Ohlsen, W. D., and Johns, O. W., *Phys. Rev.* **175,** 1091 (1968).
19. Nakato, Y., Ogawa, H., Morita, K., and Tsubomura, H., *J. Phys. Chem.* **90,** 6210 (1986).
20. Kiwi, J., and Grätzel, M., *J. Phys. Chem.* **88,** 1302 (1984).