2, gives an activation energy of 7.4 \pm 0.2 kcal/mol and a preexponential factor equal to $10^{11.1\pm0.1}$ s⁻¹. This low A factor is consistent with the highly organized transition state proposed by Bird et al.8

The rate constant of reaction 2 with 1-hexene, k_q , was obtained by analyzing, as a mixture of first- and second-order processes, the decay of the 250-nm transient in the presence of 1-hexene (HEX). A plot of the observed pseudo-first-order rate constant k_1 vs [HEX] is linear, and with $k_1 = k_1 + k_q$ [HEX], its slope yields $k_{\rm q} = 3 \times 10^5 \,{\rm M}^{-1} \,{\rm s}^{-1}$. Also, this rate constant can be obtained

(8) Bird, C. L.; Frey, H. M.; Stevens, I. D. R. J. Chem. Soc., Chem. Commun. 1967, 70, 7.

by monitoring the growth of 3 at 370 nm as a function of added HEX, with a constant [pyridine] = 2.7 mM. The addition of HEX decreases the yield of ylide (because the cycloaddition of 2 to HEX competes with ylide formation) and increases the rate of growth of 3, $k_g = k_i + k_y$ [pyridine] + k_q [HEX]. The slope of the plot of k_g vs [HEX] gives $k_q = 4.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ for the addition of 2 to 1-hexene. The difference between the k_{a} values derived from the two methods is due to the fact that the second-order component of the carbene decay was not taken into account in the kinetic analysis of the ylide growth. However, the pyridine technique provides a good estime of k_0 and is particularly useful when the absorption of the quencher prevents the direct observation of the carbene.

In Situ Photoluminescence of TiO₂ as a Probe of Photocatalytic Reactions

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The addition of unsaturated hydrocarbons such as $1-C_4H_8$ and $C_2H_5C=CH$ onto the TiO₂ catalyst causes an increase of the intensity of the photoluminescence (PL) of the catalyst as a radiative surface process from photoformed electrons and holes. The extent of the PL enhancement strongly depends on the ionization potential of the added compounds, i.e., the lower the ionization potential of the added compound, the larger the PL intensity. A parallel relationship between the enhancement of the PL of the TiO₂ by the addition of unsaturated hydrocarbons and the rate of photocatalytic hydrogenation of these compounds with H_2O on the TiO₂ catalyst suggests that these surface processes are closely associated, with both being crucially dependent on the binding of the added molecules to the TiO₂ surface.

Introduction

Solar utilization via chemical storage can be achieved by photocatalytic and/or photoelectrochemical activation of light-sensitive semiconductor surfaces.¹⁻¹⁰ The absorption of photons corresponding to the fundamental absorption band of the catalyst leads to the formation of electron-hole pairs, some of which undergo radiative decay as photoluminescence. Therefore, studies of photoluminescence (PL) in the presence of reactant molecules are expected to be useful not only in understanding the surface structure and the excited states of the catalysts but also as a probe of surface processes leading to the photochemical production of electrons and holes.¹¹⁻¹⁴ However, although TiO₂ catalysts are

(14) Anpo, M.; Kubokawa, K. J. Phys. Chem. 1984, 88, 5556. Anpo, M. Rev. Chem. Intermed. 1989, 11, 67. Anpo, M.; Kubokawa, Y. Rev. Chem. Intermed. 1987, 8, 105 and references therein.

known to exhibit high activity for decomposition of H₂O, few PL studies have been carried out in connection with photocatalysis and/or photoconductance. Along these lines, PL studies are undertaken in the present work using "standard TiO₂ catalysts" supplied by the Catalysis Society of Japan.

Experimental Section

The quartz cell used in the present study was about 30 cm long and 0.3 cm in diameter. The TiO₂ catalyst could be moved vertically between the window section and the furnace section, so that its temperature could be changed from room temperature to about 1200 K. The cell was connected to a conventional vacuum system. Ultimate vacua of 10⁻⁶ Torr were attainable. Prior to the experiments, a standard TiO₂ sample (JRC-TiO-5) (particle diameter, 0.5–1.0 μ m; BET surface area, 2.7–3.1 m²/g; purity >99.97% (impurity: Al, Fe, and Cl); crystal structure, rutile >90%) was degassed in vacuo at 723 K for 5 h, heated in pure O₂ at 723 K for 4 h, and then finally degassed at 473 K until 1 \times 10⁻⁵ Torr was reached, in order to remove carbonaceous impurities and adsorbed oxygen.¹⁵ PL spectra were measured on a Shimadzu RF-501 spectrofluorophotometer (equipped with filters to eliminate scattered light) in the temperature range from 77 to 300 K. ESR measurements were carried out at 77 K with

Honda, K.; Fujishima, A. Nature (London) 1972, 238, 37.
 Schrauzer, G. N.; Guth, T. D. J. Am. Chem. Soc. 1977, 99, 7189.
 Kraeutler, B.; Bard, A. J. J. Am. Chem. Soc. 1977, 99, 7729.
 Bard, A. J. J. Photochem. 1979, 59, 10; Science 1980, 207, 139.

⁽⁵⁾ Yoneyama, H.; Koizumi, M.; Tamura, H. Bull. Chem. Soc. Jpn. 1979, 52, 3449.

⁽⁶⁾ Kawai, T.; Sakata, T. Nature (London) 1980, 236, 474.

⁽⁷⁾ Kiwi, J.; Gratzel, M. J. Am. Chem. Soc. 1979, 101, 7214.

 ⁽⁸⁾ Sato, S.; White, J. M. J. Am. Chem. Soc. 1980, 102, 7206.
 (9) Wagner, F. T.; Somorjai, G. A. J. Am. Chem. Soc. 1980, 102, 5494.

⁽¹⁰⁾ Fox, M. A. Acc. Chem. Res. 1983, 16, 314; Top. Curr. Chem. 1988, and references therein.

Henglein, A. J. Phys. Chem. 1982, 86, 2291.
 Becker, W. G.; Bard, A. J. J. Phys. Chem. 1983, 87, 4888.
 Rossetti, R.; Brus, L. J. Phys. Chem. 1982, 86, 4470.

⁽¹⁵⁾ After these pretreatments, the surface of the TiO₂ catalyst is expected to be oxygen free and clean (of carbonaceous impurities). The same PL intensities were always obtained after these pretreatments.



Figure 1. Photoluminescence of TiO₂ at 77 K²³ in the absence (spectrum a) and presence of added O₂ (spectra b-f). Excitation wavelength = 300 nm; temperature = 77 K; amounts of added O₂ (in 10^{-6} mol/g of catalyst): (a) 0; (b) 1.1; (c) 4.7; (d) 11.8; (e) 38.2; and (f) 72-150.

a Jeol (JES-ME-1) (X-band) spectrometer. Photoreactions were carried out at 298 K using a Toshiba SHL-100UV mercury lamp ($\lambda > 280$ nm). Details of the apparatus and procedure were described previously.¹⁴

Results and Discussion

As shown in Figure 1, the standard catalyst exhibits PL at 450-550 nm when excited with light having energies larger than the band gap of the catalyst. With increased adsorption of O_2 onto the TiO₂ catalyst, the PL markedly decreases in intensity. However, the addition of excessive amounts of O₂ did not quench the PL completely, and about 15% of the PL remains unquenched under 1 atm of O₂. The intensity recovered only partially upon evacuation of the sample at 298 K. ESR measurements indicated that the addition of O_2 at 298 K onto TiO₂ led to the formation of O_2^- anion radicals adsorbed onto Ti⁴⁺ sites. It is likely that the irreversible PL quenching is attributable to the formation of O_2^- , since superoxide is thermally stable and remains on TiO₂ even after exhaustive evacuation of the catalyst at 298 K. The addition of N_2O also led to PL quenching, but with a much lower efficiency than that of O_2 . Small amounts of N_2O decomposed into N_2 and O^- through the electron transfer from the TiO₂ to N₂O molecules.16-18

On the other hand, as shown in Figure 2, the addition of increasing amounts of $1-C_4H_8$ onto the TiO₂ catalyst caused the PL to increase in intensity. Similarly, the addition of various unsaturated hydrocarbons (C_3H_6 , $C_2H_5C=CH$, $CH_3C=CH$, C_2H_4 , CH=CH), H_2O , and H_2 enhanced the observed PL. As shown in Figure 3, the extent of PL enhancement strongly depends on the ionization potential of the added compounds: i.e., the lower the ionization potential of the added compound, the larger the PL intensity. The PL intensity was changed only negligibly by the addition of N_2 .

These results suggest that the formation of negatively charged adducts (via electron capture) on the TiO_2 surface causes PL quenching, while the formation of positive adducts (via hole trapping) results in an enhancement of the PL. These PL changes are accommodated by the dead-layer model proposed by Ellis et al. to explain PL enhancement of n-CdS and n-CdSe by amines and unsaturated hydrocarbons, permitting the semiconductor's depletion width to be tracked between additions.¹⁹



Figure 2. Photoluminescence spectra of TiO₂ at 77 K²³ in the absence (spectrum a) and presence of added 1-C₄H₈ (spectra b-f). Excitation wavelength = 300 nm; temperature = 77 K; amounts of added 1-C₄H₈ (in 10⁻⁶ mol/g of catalyst): (a) 0; (b) 4.7; (c) 16.2; (d) 25.7; (e) 38.2; and (f) 72-148.



Figure 3. Effect of additive ionization potentials on the photoluminescence intensity $(-\bullet-)$ and the rate of the photocatalytic hydrogenation of the added unsaturated hydrocarbons with H₂O on TiO₂ (-o-). I_0 and I_{max} are maximum photoluminescence intensities, respectively, under vacuum (or in N₂) and in the presence of added compounds: (1) 1,3butadiene; (2) 1-butene; (3) propene; (4) 1-butyne; (5) 1-propyne; (6) ethylene; and (7) acetylene) (photoluminescence spectra were recorded at 77 K. Photocatalytic reactions were carried out at 298 K.

As described previously,^{2,20-22} UV irradiation of TiO₂ which contains a sufficient amount of H₂O in the presence of an unsaturated hydrocarbon such as CH₃CH=CH₂, C₂H₅=CH, CH₃C=CH, CH₂=CH₂, or CH=CH leads to photocatalytic hydrogenation accompanied by the fission of the C=C or C=C bond of the reactant. In addition to the formation of these products, oxygen-containing products (such as C₂H₅COCH₃ and C₂H₅CHO) as well as CO and CO₂ were detected. The rates of these photocatalytic hydrogenation reactions were found to increase with decreasing ionization potential of the reactants, Figure 3.

A parallel relationship between the enhancement of PL of TiO_2 by the addition of unsaturated hydrocarbons and the rate of

⁽¹⁶⁾ Cunningham, J.; Penny, A. L. J. Phys. Chem. 1974, 78, 870.

⁽¹⁷⁾ Tanaka, K.; Blyholder, G. J. Phys. Chem. 1972, 76, 1807.

⁽¹⁸⁾ Che, M.; Tench, A. J. Adv. Catal. 1982, 31, 77.

 ⁽¹⁹⁾ Meyer, G. J.; Lisensky, G. C.; Ellis, A. B. J. Am. Chem. Soc. 1988, 110, 4914; *Ibid.* 1989, 111, 5146; In *Photochemistry on Solid Surfaces*; Anpo, M., Matsuura, T., Eds.; Elsevier: Amsterdam, 1989; p 388.

⁽²⁰⁾ Boonstra, A. H.; Mutsaers, C. A. H. A. J. Phys. Chem. 1975, 79, 2025.

⁽²¹⁾ Anpo, M.; Aikawa, N.; Kodama, S.; Kubokawa, Y. J. Phys. Chem. 1984, 88, 2569. Anpo, M.; Yabuta, M.; Kodama, S.; Kubokawa, Y. Bull. Chem. Soc. Jpn. 1986, 59, 259.

⁽²²⁾ Anpo, M.; Aikawa, N.; Kubokawa, Y. J. Phys. Chem. 1984, 88, 3998.
(23) PL experiments were also carried out in the gas phase at 300 K. We could obtain the same results as in the present experiments. However, the yields of PL were very low and the experimental errors became much larger than those at 77 K.

photocatalytic hydrogenation of these same unsaturated hydrocarbons with H₂O on TiO₂ suggests that these photoinduced surface processes are closely associated, with both being crucially dependent on the binding of the added molecules to the TiO_2 surface. In other words, the formation of adsorbed cations derived from oxidation of the reactant on the TiO₂ catalytic surface plays a significant role in determining the reactivity of the photogenerated electron-hole pairs. Further work is in progress.

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High-T_c Superconductors and Weighted Harmonic Mean Electronegativities

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A new electronegativity scale based on Mulliken's concept is suggested which indicates systematic changes in the superconductive critical temperature (T_c) with composition for some high- T_c oxides. By this scale the optimum electronegativity seems to exist between 4.7 and 4.9 eV, which is a very narrow range compared to that for low-T_c binary alloys of normal stoichiometry as well as A15 type crystal structure.

Introduction

Classification methods that distinguish what is or what is more superconductive from what is not or what is less superconductive can be useful in the search and development of new superconductive materials as well as in the studies to unravel the intricacies of high- T_c oxides. Among the more conceptually simple and easily applicable methods is the one due to Mathias,¹ which has already been utilized exhaustively for the design of relatively low $T_{\rm c}$ superconductors.

Recently, some reports²⁻⁴ have indicated systematic correlations between electronegativity and the values of T_c for superconductive elements,^{2,4} binary alloys,⁴ and high- T_c oxides.³ A brief summary of their results is in order. Superconductive elements² have electronegativity values that are concentrated within a range near the center of Pauling's scale (1.3-1.9) whereas on the same scale they lie between 2.5 and 2.65 for the high- T_c oxides³ based on a particular method to calculate average electronegativities. In our case,⁴ we have chosen to utilize Mulliken's definition⁵ of the electronegativity because of two main reasons. It is the most physically sound compared to others (Pauling, Allred-Rochow, Sanderson)⁶ as can be concluded from a recent extensive review. Also, Mulliken's concept is consistent with quantum mechanics as shown through the density-functional formalism.⁸ Furthermore, the concept of electronegativity equilibration in harmony with the density-functional theory9 was incorporated into our formulation. The results⁴ were that the optimum electronegativity for superconductive metal elements and binary alloys is about 4 eV, which is at the midpoint in the span of metal electronegativities.

- Luo, Q-G.; Wang, R.-Y. J. Phys. Chem. Solids 1987, 48, 425.
 Asokamani, R.; Manjula, R. Phys. Rev. 1989, B39, 4217.
 Ichikawa, S. J. Phys. Chem. Solids 1989, 50, 931.

- Mulliken, R. S. J. Chem. Phys. 1934, 2, 782.
- (6) See for example: Huheey, J. E. Inorganic Chemistry; Harper and Row: New York, 1978.
- (7) Sen, K. D.; Jorgensen, C. K. Electronegativity; Springer-Verlag: New York, 1987.
 - (8) Hohenberg, P.; Kohn, W. Phys. Rev. 1964, B136, 864.
 (9) Plitzer, P.; Weinstein, H. J. Chem. Phys. 1979, 71, 4218.

At a first glance, application of electronegativity concepts to structurally complex materials like the high- T_c oxides appears to be a formidable task. In the following however a new electronegativity scale is presented that reflects systematic trends of $T_{\rm c}$ with composition of the oxides.

Weighted Harmonic Mean Electronegativity

According to Mulliken,⁵ the electronegativity of an atom χ_{M} is the arithmetic average of the first ionization potential (IP) and the electron affinity (EA)

$$\chi_{\rm M} = \frac{1}{2}({\rm IP} + {\rm EA})$$
 (1)

This definition, in spite of its theoretical rigor and simplicity, had to wait until quite recently to be utilized extensively for various applications because of the lack of reasonably accurate experimental values for the electron affinities. Thus, from the recommended EA values in a recent critical review¹⁰ and almost universally agreed upon values of the first ionization potentials,¹¹ we can now calculate the Mulliken electronegativities for the main-group elements and for the three long series including the transition metals.

When two atoms of different electronegativities are brought together, charge transfer occurs until an equilibrium is reached at which point the binary system attains a unique electronegativity χ_{eq} . This intuitive picture originally suggested by Sanderson¹² is shown to be consistent with a quantum mechanical calculation as mentioned above. An analogy can be made to the equilibration of Fermi levels when two solids come into contact. We have recently reported¹³ that when the energy of an atom is expressed

- (12) Sanderson, R. T. Science 1955, 121, 207.
- (13) Wilson, M. S.; Ichikawa, S. J. Phys. Chem. 1989, 93, 3087.
 (14) Torardi, C. C.; Subramanian, J. C.; Calabrese, J. C.; Gopalakrishnan,
- J.; McCarron, E. M.; Morrissey, K. J.; Askew, T. R.; Flippen, R. B.; Chowdry, U.; Sleight, A. W. Phys. Rev. 1988, B38, 225.
- (15) Wu, M. K.; Ashburn, C. J.; Rorng, C. J.; Hor, P. H.; Meng, R. L.; Gao, L.; Huang, A. J.; Wang, Y. O.; Chu, C. W. Phys. Rev. Lett. 1987, 58, 908.

⁽¹⁾ Mathias, B. T.; Geballe, T. H.; Compton, V. B. Rev. Mod. Phys. 1963, 35, 1

⁽¹⁰⁾ Hotop, H.; Lineberger, W. C. J. Phys. Chem. Ref. Data 1985, 14, 731

⁽¹¹⁾ CRC Handbook of Chemistry and Physics, 62nd ed.; CRC Press: Boca Raton, FL, 1981.