Photocatalysis on Native and Platinum-Loaded TiO_2 and ZnO Catalysts — Origin of Different Reactivities on Wet and Dry Metal Oxides —

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Substantial differences in photocatalytic reactivity were observed on powdered TiO_2 and ZnO, both Pt-loaded and unloaded, in the photocatalytic hydrogenation of $CH_3C{\equiv}CH$ and C_3H_6 in the presence of H_2O. Similar reactivity was observed, however, in the photocatalytic oxidation of i-C_4H_8 and C_3H_6 by O_2 on these same catalysts. Photoluminescence of TiO_2 and ZnO in the presence and the absence of H_2O and/or O_2 indicate that H_2O causes a downward band bending to increase the efficiency of recombination of photogenerated electrons and holes, with a greater effect being observed on ZnO than on TiO_2. These results, together with the direct detection of reaction intermediates by ESR, are rationalized by differences in the yields of the photogenerated intermediates, i. e., $\dot{H}$ (formed from trapped electrons) and $\dot{O}H$ (formed from trapped holes). The steady state concentrations of these intermediates depend on the degree of the positively-charged adducts on the surfaces of these oxides. The addition of O_2 causes an upward band bending of the oxide and suppresses recombination of photo-generated electrons and holes, by formation of negatively-charged surface adducts. With similar degrees of band bending, TiO_2 and ZnO produce almost the same photocatalytic reactivities as are observed for these oxides as dry systems.

Solar utilization via chemical storage can be achieved by photocatalytic and/or photoelectrochemical activation of light-sensitive semiconductor surfaces. Recent studies of photocatalysis have been focused on colloidal semiconductors,[1-4] on extremely small-sized particles in which size quantization effects are expected,[5-11] on highly dispersed well-defined supported catalysts,[12-20] and on various binary metal oxides.[21-28] Detection of the transient processes involving electron and/or energy transfer at the interfaces of the semiconducting materials has been recently contributed to a complete understanding of the true nature of the photocatalysis.[29-41]

Most photocatalytic studies on powdered semiconductors have been concerned only with analysis of reaction products and yields. These studies were mainly carried out as solid-liquid systems, where various electrochemical measurements are relatively easy but direct measurements of the intermediate species by ESR and the excited state of catalysts by photochemical techniques are difficult, compared with those in the solid-gas systems. In fact, besides a small number of mechanistic studies,[39,41-47] few photoelectrochemical measurements at the liquid-solid interface have characterized reaction intermediates or identified the excited state and/or primary processes of photocatalysis. Such mechanistic investigations would be much easier at the gas-solid interface, as has been shown in our earlier works.[4,12]

Most mechanistic studies of metal oxides have investigated on TiO_2,[1-4,12] because of its high activity and stability. A small number have been undertaken on ZnO,[46,1,48-51] although it is very similar electrochemically to TiO_2. Recently, in a preliminary study, a substantial difference in the photoreactivities of powdered TiO_2 and ZnO for the activation of H_2O and/or OH groups on the surface of these oxides has been reported despite similar reactivity for the activation of O_2 and/or lattice oxygen ions on these surfaces.[1] A detailed investigation of this different photoreactivity might clarify photocatalysis on these semiconducting materials.

In the present work we compare photocatalytic reactions on powdered TiO_2 and ZnO in the solid-gas systems in the presence (wet system) and the absence of H_2O (dry system), the effect of Pt loading on the photoreactivities of these oxides, the origin of their different reactivities, and direct measurements of the reaction intermediates by ESR and the excited state of catalysts by photoluminescence spectroscopy.

Experimental

TiO_2 (rutile) (BET surface area; 8.0 $m^2\,g^{-1}$, average particle size; 1000—2000 Å) was supplied by Ishihara Sangyo Kaisha, Ltd. Kadox-25 ZnO powder (BET surface area; 8.5 $m^2\,g^{-1}$, average particle size; 1000—1500 Å) was used, because it has almost the same surface area and particle size to those of TiO_2 used. Pt-loaded catalysts were prepared by mixing the desired amount of TiO_2 (or ZnO) and Pt black powder (2.0 wt%) followed by thorough grinding in an agate mortar. $CH_3C{\equiv}CH$, C_3H_6, and i-C_4H_8 were extra pure grade from the Takachiho Kogyo Co., used without further purification. $^{18}O_2$ (90%, E. Merck Co.) was used. Deionized twice-distilled water was degassed by alternate freezing and thawing in vacuo.

The quartz cell used in the present study was about 10 cm long and 5.0 cm in diameter with a total volume of about 300 cm^3. The catalyst could be moved between the window section and the furnace section, so that its temperature could be raised from room temperature to about 1200 K. The cell was connected to a conventional vacuum system. Prior to the reaction, catalysts were degassed at 773 K for 5 h, heated in O_2 at the same temperature for 5 h, and then finally evacuated at 623 K to 10^{-6} Torr (1 Torr=133.322 Pa). After evacuation of the catalyst, water vapor (i. e., wet system) or oxygen (i. e., dry system) was introduced onto the catalyst, followed by the reactant molecules at 298 K. UV irradiation was carried out with a 75-W high-pressure mercury lamp (Toshiba SHL 100UV) through a cut-off and a water filter (λ>280 nm) at 298 K. The reaction products were collected in cold traps.

Analysis of the reaction products was carried out by gas chromatography. Quantum yields were measured at 300 nm by potassium trioxalatoferrate actinometry. Isotopic analysis of O_2 was carried out with a quadrupole mass spectrometer. ESR measurements were carried out at 77 K with a JEOL ME-1 (X-band). UV irradiation for ESR measurments was carried out using a 500-W high-pressure mercury lamp with a color filter (λ>280 nm) in a ESR cavity. Diphenylpicrylhydradyl (DPPH) was used for g values and sweep calibration. Photoluminescence spectra were measured by using a Shimadzu RF-501 spectrofluorophotometer equipped with filters to eliminate scattered light at 298 and 77 K. The amount of desorbed H_2O from the catalysts (TPD spectra) was determined by measuring the pressure of desorbed H_2O as the temperature was increased step by step from 273 to 873 K. A monolayer of H_2O had been adsorbed previously on the catalysts. Analysis of the X-ray diffraction lines of the catalysts showed that the catalysts consist of only pure rutile-type TiO_2 crystallites and pure ZnO, respectively. The particle diameters were determined by X-ray diffraction and/or transmission electron microscopy. Details of the experiments were described in the previous papers.[52–55)]

Results and Discussion

1. Photocatalysis on TiO_2 and ZnO Catalysts in Wet Systems. Figure 1 shows the observed differences in the photocatalytic hydrogenation yields for the reactions of $CH_3C{\equiv}CH$ with H_2O (wet system) on Pt-free powdered TiO_2 (TiO_2), Pt-loaded powdered TiO_2 (Pt/TiO_2), Pt-free powdered ZnO (ZnO), and Pt-loaded powdered (Pt/ZnO) catalysts at 298 K. The initial rates and quantum yields of these reactions are described in Table 1. Table 2 includes these values

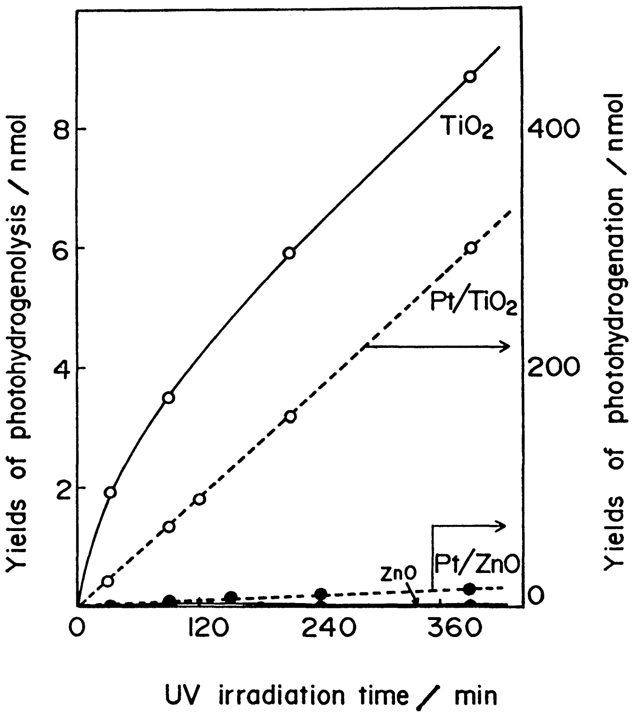

Fig. 1. Photocatalytic hydrogenation of $CH_3C{\equiv}CH$ with H_2O on Pt/TiO_2, TiO_2, Pt/ZnO, and ZnO at 298 K. (UV irradiation: 280 nm, 3 Torr C_3H_4, 8 Torr H_2O,)

Table 1. Comparison of the Rates and Quantum Yields of Photohydrogenation of $CH_3C{\equiv}CH$ with H_2O on TiO_2, Pt/TiO_2, ZnO, and Pt/ZnO Catalysts at 298 K[a)]

Catalysts	Major products[b)]/10^{-9} mol m^{-2} h^{-1}						
	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	CO	CO_2
TiO_2	0.10	0.018	0.57	0.013	0.02	1.03	5.75
Pt/TiO_2	0.17	0.174	0.28	7.57	0.83	1.885	8.72
Quantum yields[c)]	—	—	0.004	0.114	—	0.028	0.13
ZnO	0.0017	Trace	0.0094	Trace	Trace	0.034	0.107
Pt/ZnO[d)]	0.002	0.0023	0.0021	0.153	0.197	0.040	0.201

a) The pressures of $CH_3C{\equiv}CH$ and H_2O were 3 and 8 Torr, respectively. b) CH_3CHO, CH_3COCH_3, $CH_3COC_2H_5$ were detected as minor oxidation products. c) Quantum yields were determined at 350±10 nm on Pt/TiO_2 at 298 K. Quantum yield=(number of photoformed product)/(number of incident photons). d) Quantum yields were too low to determine on ZnO.

Table 2. Comparison of the Rates and Quantum Yields of Photohydrogenation of C_3H_6 with H_2O on TiO_2 and Pt/TiO_2, Catalysts at 298 K[a]

Catalysts	Major products[b]/10^{-9} mol m^{-2} h^{-1}					
	CH_4	C_2H_4	C_2H_6	C_3H_8	CO	CO_2
TiO_2	0.21	Trace	0.67	Trace	0.76	4.33
Pt/TiO_2	0.17	Trace	0.53	5.00	1.07	6.42
Quantum yields	—	—	0.0075	0.071	0.015	0.091

a) The pressures of C_3H_6 and H_2O were 3 and 8 Torr, respectively. b) CH_3CHO, CH_3COCH_3, and $CH_3COC_2H_5$ were detected as minor oxidation products. c) Quantum yields were determined at 350±10 nm on Pt/TiO_2 at 298 K. Quantum yield=(number of photoformed product)/(number of incident photons). Rates of photohydrogenation on ZnO were too low to follow the kinetics.

for the results of the photohydrogenation reaction of C_3H_6 with H_2O on Pt-loaded and unloaded TiO_2. The rates of the photocatalytic hydrogenation of C_3H_6 with H_2O on ZnO and Pt/ZnO catalysts were too low to follow their kinetics. The major products of the photocatalytic hydrogenation of $CH_3C{\equiv}CH$ and C_3H_6 with H_2O on TiO_2 and on ZnO were C_2H_6 as hydrogenation product accompanied by the fission of the carbon-carbon bond of $CH_3C{\equiv}CH$ and C_3H_6, i. e., hydrogenolysis (CH_4 as minor product), and CO_2 as oxidation product. Ketones and aldehydes were also detected as minor photooxidation products.

The product distribution in the photocatalytic hydrogenolysis is in good agreement with that observed on TiO_2 catalysts,[52–55] which has been attributed to a closely spaced photogenerated electron-hole pair, i. e., Ti^{3+}-$\dot{O}H$ pair species. These electron-hole pairs can interact with $CH_3C{\equiv}CH$ adsorbed on the surface to form the carbenes and/or oxygen-containing compounds via carbon-centered radicals such as $\dot{C}H$ and $CH{\equiv}\dot{C}$ formed in a manner similar to that described previously.[52,54,55]

On the other hand, as shown in Table 1 and Fig. 1, on Pt/TiO_2 and Pt/ZnO, where the photoelectrochemical mechanism is operating, the major product was C_3H_6: that is, hydrogenation dominated over carbon-carbon bond fission while producing CO_2 as oxidation product. The rates for the photocatalytic hydrogenation are markedly enhanced on both TiO_2 and ZnO by the presence of Pt as a co-catalyst, Table 1. The rates of photocatalytic hydrogenolysis on TiO_2 and hydrogenation on Pt/TiO_2 of $CH_3C{\equiv}CH$ with H_2O are much higher than those on ZnO and Pt/ZnO, respectively, with nearly the same conversion being observed on the Pt-loaded and native systems. With TiO_2 and ZnO, the rates of oxidation are much higher than that of the hydrogenation. However, with Pt/TiO_2 and Pt/ZnO, there is no marked difference between the rates, supporting our previous assertion that photoreactions on Pt-loaded TiO_2 and ZnO are much more catalytic than those on Pt-free TiO_2 and ZnO.[53]

Figure 2 shows a temperature-programmed desorption (TPD) spectra for desorption of H_2O from TiO_2 and ZnO after the adsorption of a monolayer of H_2O at 298 K. The amounts of water desorbed from TiO_2 and ZnO in the temperature range from 273 to 673 K are almost the same, whether native or Pt-loaded. Thus, the observed differences in rates of photocatalytic reactions do not correlate with the steady state adsorption of water.

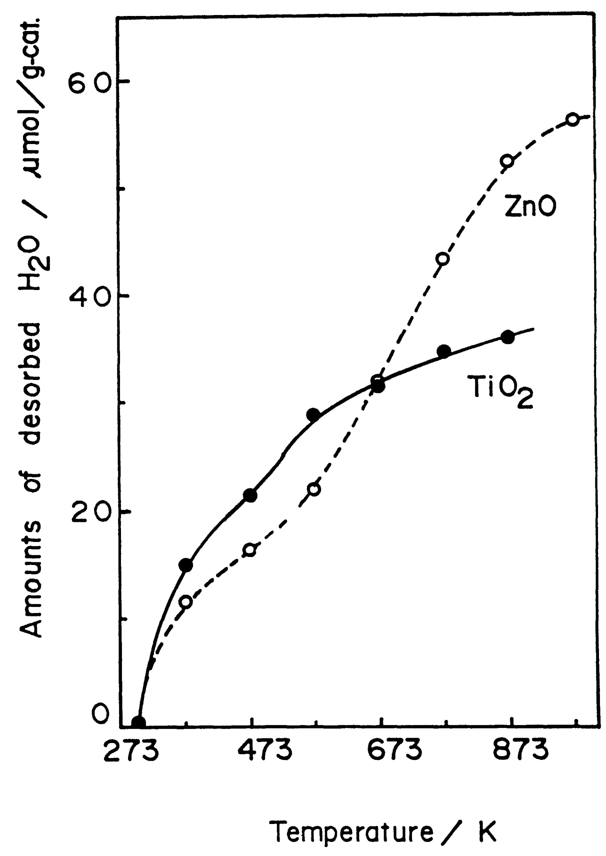

Fig. 2. Amounts of desorbed H_2O from TiO_2 and ZnO. (A monolayer of H_2O had been adsorbed previously on the oxides at 298 K.)

The efficiency of photoreactions on TiO_2 is higher than that on ZnO by a factor of at least 40, irrespective of Pt loading. In these photohydrogenation reactions on TiO_2 (or ZnO) in the presence of adsorbed H_2O, it is likely that both $\dot{H}$ and $\dot{O}H$ radicals are generated,[12,52–54] Eqs, 1 and 2, respectively, since a water dissociation preequilibrium $H_2O \rightleftarrows H^+ + OH^-$ is established on oxides.[52] Therefore, photogenerated electrons (or Ti^{3+}) are trapped by protons supplied from the acidic groups at the specific surface sites. Photogenerated holes (or O^-) are trapped at basic surface sites, though the nature of the basic OH^- groups associated with the oxidation is still unclear.

$$H^+ + e^- \ (Ti^{3+}) \longrightarrow \dot{H} + Ti^{4+} \qquad (1)$$

$$OH^- + h^+ \ (O^-) \longrightarrow \dot{O}H + O^{2-} \qquad (2)$$

On the Pt-free TiO_2 and ZnO, both $\dot{H}$ and $\dot{O}H$ radicals are formed on these oxides at sites close to each other, their proximity resulting in photocatalytic hydrogenolysis accompanied by the carbon-carbon bond fission, but not hydrogenation.[52–54] On the Pt-loaded TiO_2 and ZnO, however, enhancement of electron trapping by adsorbed protons on Pt results in more efficient charge separation.[53] Thus, the marked increase in the rate of photohydrogenation on Pt/TiO_2 and Pt/ZnO probably arises from addition of H atoms to $CH_3C{\equiv}CH$ and C_3H_6 on Pt particle sites but not on TiO_2 or ZnO. This results in a high efficiency for photocatalytic hydrogenation, and a much better balanced contribution of photogenerated electrons and holes to the surface reactions, i. e., a much more catalytic reactivity. The similarity in the product distribution shown in Fig. 1 and Table 1 clearly suggests that the reaction mechanisms operative on ZnO are the same as those on TiO_2, except for the much lower yields.[1]

2. Photocatalysis on TiO_2 and ZnO Catalysts in Dry Systems. UV irradiation of TiO_2 and ZnO in the presence of the mixtures of hydrocarbons and oxygen leads to the oxidation of these compounds.[1,51,56] Figure 3 shows the observed differences in the yields of the photocatalytic oxidation of i-C_4H_8 by O_2 (i. e., dry system) on Pt-free TiO_2, Pt/TiO_2, Pt-free ZnO, and Pt/ZnO catalysts at 298 K.[1] The rates and quantum yields of photooxidation of i-C_4H_8 and C_3H_6 by O_2 on these Pt-loaded and native catalysts are shown in Table 3. The major products of the photocatalytic oxidation of i-C_4H_8 are CH_3COCH_3 and CO_2 on all four catalysts, but products are formed with different rates and selectivities. In the photocatalytic oxidation of C_3H_6, various oxygen-containing compounds such as CH_3COCH_3, C_2H_5CHO and CH_3OH, in addition to the formation of CO_2, are obtained. The efficiency of TiO_2 for the photocatalytic oxidation of i-C_4H_8 and C_3H_6 is about 1.2—2 times higher than that of ZnO. These values are smaller than those obtained in wet systems by at least an order of magnitude.

UV irradiation of TiO_2 and ZnO in the presence of isotopically-labelled O_2 leads to the photocatalytic oxygen isotopic exchange,[56,57] (Fig. 4). The degassing temperature and the presence of H_2O influence the

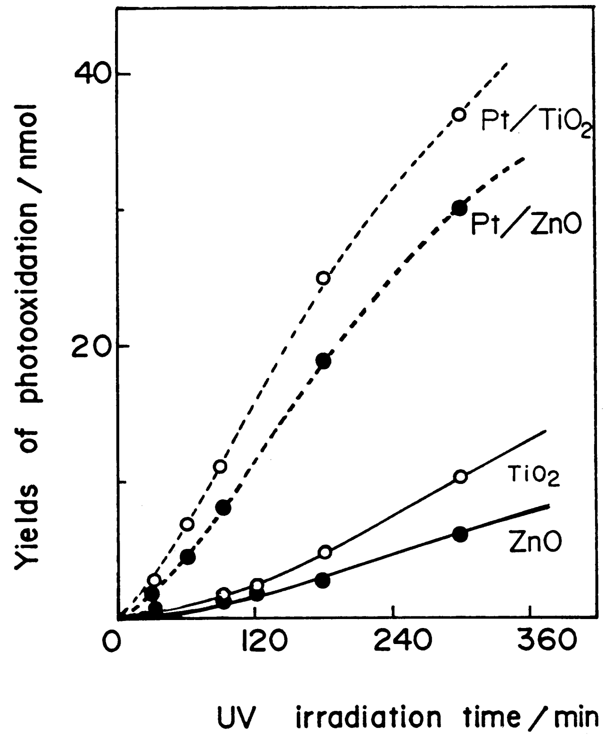

Fig. 3. Photocatalytic oxidation of i-C_4H_8 with O_2 on dry Pt/TiO_2, TiO_2, Pt/ZnO, and ZnO at 298 K. (UV irradiation: 280 nm, 6 Torr O_2, 3 Torr i-C_4H_8.)

Table 3. Comparison of the Rates and Quantum Yields of Photooxidation of i-C_4H_8 and C_3H_6 with O_2 on TiO_2, Pt/TiO_2, ZnO, and Pt/ZnO Catalysts at 298 K

Catalyst	Major products/10^{-9} mol m^{-2} h^{-1}					
	Photooxidation of i-C_4H_8 [a]		Photooxidation of C_3H_6 [b]			
	CO_2	CH_3COCH_3	CO_2	CH_3COCH_3	C_2H_5CHO	CH_3OH
TiO_2	2.50	0.881	3.1	0.557	0.16	0.52
Pt/TiO_2	45.1	1.863				
ZnO	1.31	0.567	1.92	0.36	0.11	0.28
Pt/ZnO	43.6	1.478				

a) The pressures of i-C_4H_8 and O_2 were 3 and 6.0 Torr, respectively. b) The pressures of C_3H_6 and O_2 were 1 and 3.0 Torr, respectively. c) The experiments of photooxidation of C_3H_6 by O_2 on Pt/TiO_2 and Pt/ZnO catalysts were not carried out yet.

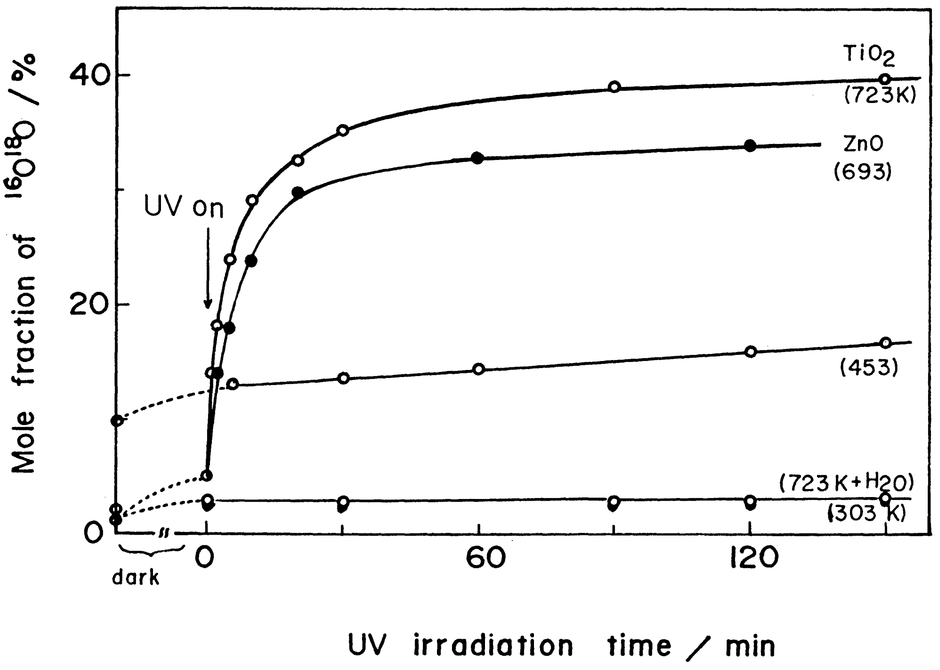

Fig. 4. Photocatalytic oxygen isotopic exchange on TiO_2 and ZnO and the effect of adsorbed H_2O on the exchange reaction on TiO_2 at 298 K. (UV irradiation: 280 nm, value in parenthesis indicates the degassing temperature of the catalyst.)

observed rates of exchange. There is only a small difference in reactivity between TiO_2 and ZnO, the reactivity of TiO_2 being higher than that of ZnO by only 1.5—2 times. Adding H_2O to the TiO_2 catalyst, which had been deggassed at 723 K, the surface OH groups markedly suppresses this reaction.

Both photocatalytic oxygen isotopic exchange and photooxidation of alkenes with O_2 on dry TiO_2 and ZnO probably proceed via O_3^- and O_2^- anion radicals, Eqs. 3 and 4:[41,42,56–58]

$$O_2 + h^+ (O^-) \longrightarrow O_3^- \quad (3)$$

$$O_2 + e^- (Ti^{3+}) \longrightarrow O_2^- \text{-} Ti^{4+} \quad (4)$$

3. Measurements of Reaction Intermediates. UV irradiation of TiO_2 in the presence of O_2 leads to the formation of O_3^- anion radicals with high efficiency, together with the formation of O_2^- anion radicals, (Fig. 5). The ESR signal assigned to O_3^- is obtained as a difference spectrum by subtracting the spectrum before irradiation from that observed after irradiation at 77 K.[54,56] The addition of O_2 to TiO_2 led to the formation of O_2^- species. The photogenerated O_3^- radicals were also observed by ESR at 77 K when ZnO was UV-irradiated in the presence of O_2. O_3^- anion radicals are probably formed via the reaction of O_2 with photogenerated O^-. This species might be formed by hole trapping on the lattice O^{2-} ions as mentioned above (i. e., reaction (3)). In the absence of O_2, the O^- species can be detected by ESR at 77 K under UV irradiation of ZnO, (Fig. 6).[59] O^- is not detected directly on TiO_2 by ESR, probably because of

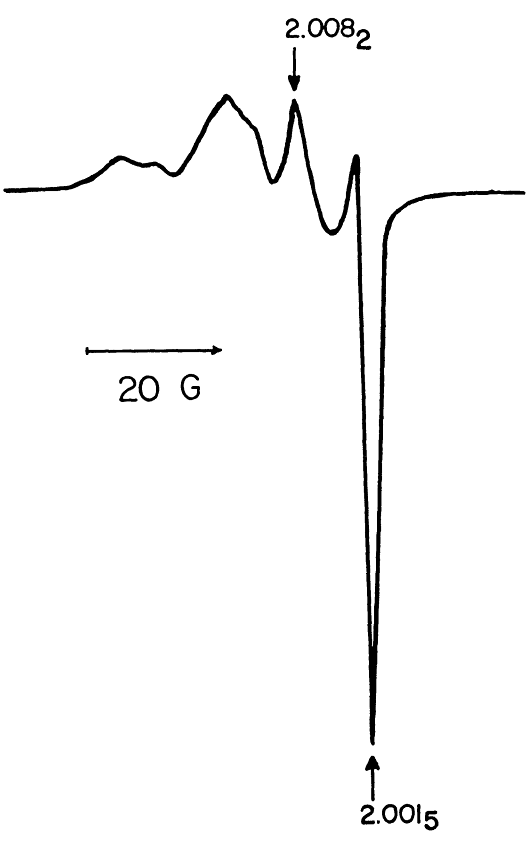

Fig. 5. ESR spectrum of the photogenerated O_3^- anion radical on TiO_2 at 77 K. (UV irradiation and ESR measurments were carried out at 77 K in the presence of O_2.)

its short lifetime even at 77 K and/or incomplete removal of the degeneracy of the p-orbitals in this species. Photogenerated electrons trapped as Ti^{3+} (or Zn^{+}) are directly associated with the photogeneration of O_2^- at Ti^{4+} sites of TiO_2 (or Zn^{2+} ions of ZnO), (Eq. 4).

In the presence of H_2O on TiO_2 and ZnO (wet systems), however, neither O_2^- nor O_3^- anion radicals could be longer detected. On extremely small TiO_2 particles (about 50 Å, and BET surface area 800 $m^2 g^{-1}$) the formation of $\dot{O}H$ radicals was detected by UV irradiation of the TiO_2 in the presence of a monolayer of H_2O.⁶⁰⁾ With the present TiO_2 catalyst (2000 Å and BET surface area 8.0 $m^2 g^{-1}$), the detection of the photoformed $\dot{O}H$ radicals was not successful because of its lower photoactivity. Formation of these $\dot{H}$ and $\dot{O}H$ radicals may have occurred on these wet systems in lieu of the formation of O_2^- and O_3^-.

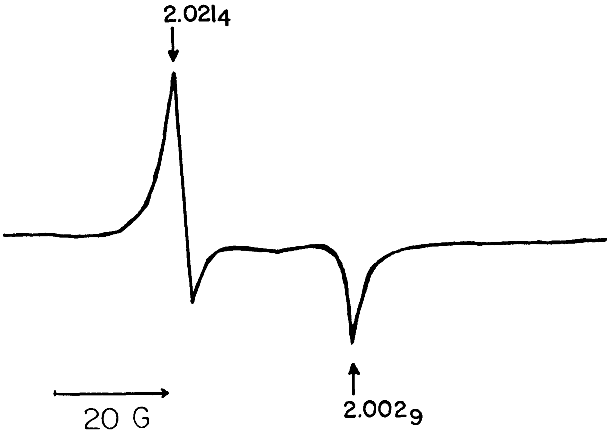

Fig. 6. ESR spectrum of the photo-generated O^- anion radical (hole trapped centers) of ZnO at 77 K. (UV irradiation and ESR measurments were carried out at 77 K in vacuo.)

4. Photoluminescence Behaviors of TiO_2 and ZnO in Dry and Wet Systems. ZnO used in the present work exhibits a high yield photoluminescence when excited with the band-gap light (about 3.2 eV=380 nm).⁵⁹⁾ Figure 7 shows the photoluminescence spectrum of ZnO (1) at 298 K and the effect of the addition of H_2O (2—4). The addition of H_2O leads to an increase of the intensity of the photoluminescence, depending on the amounts of adsorbed H_2O. As in a previous study,⁶¹⁾ the addition of $CH_3C{\equiv}CH$ or H_2O onto the TiO_2 led to an enhanced photoluminescence but the magnitude of the enhancement was much smaller than that on ZnO. That is, the addition of excess H_2O led to the 1.5—2.0 times enhancement of the photoluminescence of ZnO, while on TiO_2 it was only 1.1—1.2 times.

The addition of O_2 to ZnO leads to a decrease of the intensity of the photoluminescence, its extent depending on the amounts of added O_2, Fig. 8. As reported previously,⁶¹⁾ the addition of O_2 to TiO_2 also led to

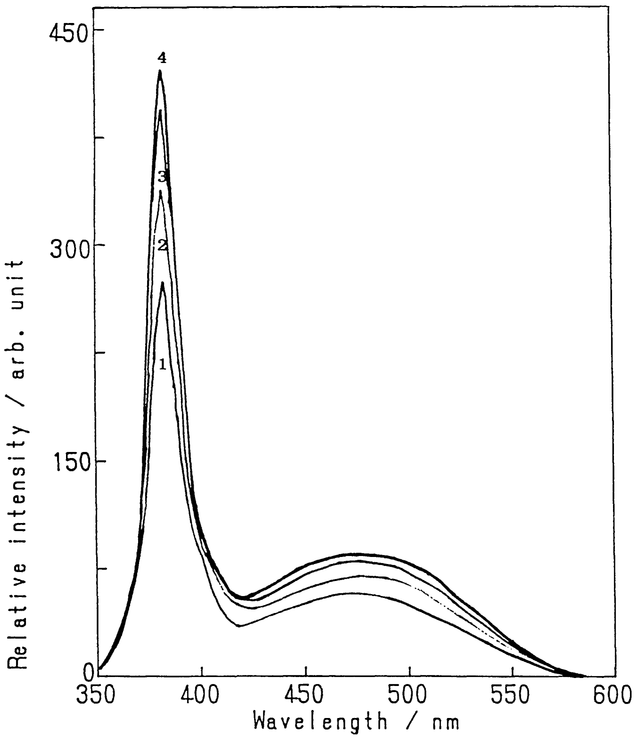

Fig. 7. Effects of H_2O on the photoluminescence of ZnO at 298 K. (Pressure of added H_2O in Torr, 1: 0.0, 2: 0.5, 3: 18, 4: excess amounts.)

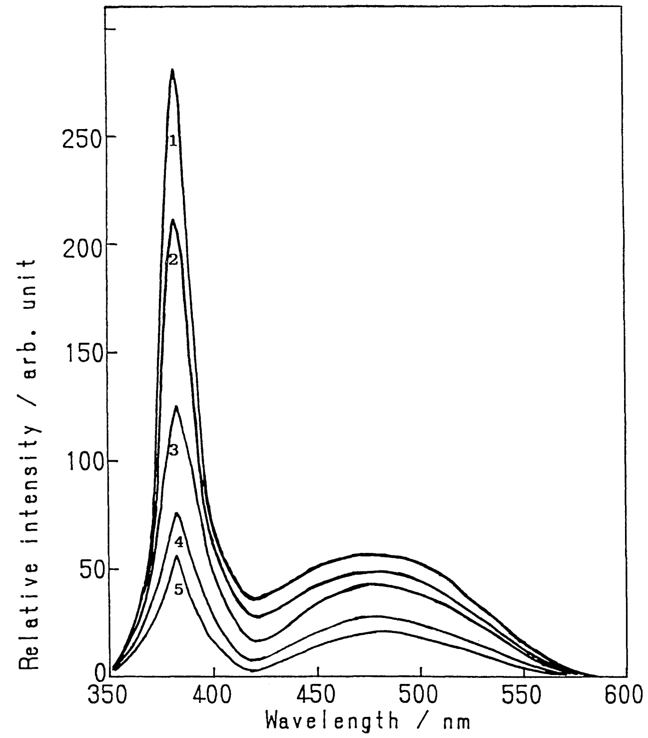

Fig. 8. Effects of O_2 on photoluminescence of ZnO at 298 K. (Pressure of added O_2 in Torr, 1: 0.0, 2: 0.5, 3: 3.5, 4: 12.0, 5: 20 or excess amounts.)

photoluminescence quenching. The addition of 3—10 Torr O_2 (even excess O_2) to TiO_2 and ZnO led to 80—95% quenching of their photoluminescence almost equally on the two oxides, though the initial yield of photoluminescence of TiO_2 is much lower than that of ZnO.

The mechanisms for the enhancement and quenching of the photoluminescence of the powdered semiconductors such as CdS and TiO_2 by added molecules are recently well explained by the models of Ellis et al.62—64) and Anpo and Fox et al.61) The formation of negatively-charged adducts (via electron capture) on the surfaces of semiconductors such as TiO_2 and CdS causes photoluminescence quenching, while the formation of positively-charged adducts (via hole trapping) results in an enhancement of the photoluminescence.

Bard et al.65) have shown that the photoluminescence quenching, photoinduced oxygen adsorption, and photodecomposition observed with ZnS particles are very sensitive to surface effects and concluded that the photoluminescence can be used as a probe of electron-hole surface processes. In fact, recently, Anpo and Fox et al.61) have found a parallel relationship between the enhancement of photoluminescence of TiO_2 by the addition of unsaturated hydrocarbons and the rates of photocatalytic hydrogenation of those same unsaturated hydrocarbons by H_2O on TiO_2. Thus, these photoinduced surface processes are closely associated with, both depending crucially on the binding of the added molecules to the TiO_2 surface. The results obtained on TiO_2 and CdS clearly suggest that the formation of adsorbed charged species plays a significant role in determining the reactivities of the photogenerated electron-hole pairs on the semiconductors.

Consequently, as shown in Fig. 9, these results suggest that the addition of H_2O and/or $CH_3C{\equiv}CH$ onto the TiO_2 and ZnO causes structural changes in surface band bending to increase the efficiency of recombination of the photogenerated electrons and holes, resulting in an enhancement of the photoluminescence, with larger effects being observed on ZnO than on TiO_2. On the other hand, the addition of O_2 onto these photocatalysts caused a suppression of the efficiency of recombination of the photogenerated electrons and holes (i. e., better charge separation), resulting in a quenching of the photoluminescence to about the same extent on TiO_2 and ZnO (Excess O_2 leads to the almost complete quenching of the photoluminescence.). Although the details are not clear at present, this photoluminescence behaviour is probably associated with the different electronic structures of the TiO_2 and ZnO surfaces, since Ti^{4+} and Zn^{2+} ions can play a significant role in forming surface adducts.

The nature of the photocatalytic action of TiO_2 and ZnO is the same for both Pt-loaded and native systems, respectively, but large differences in reactivities are

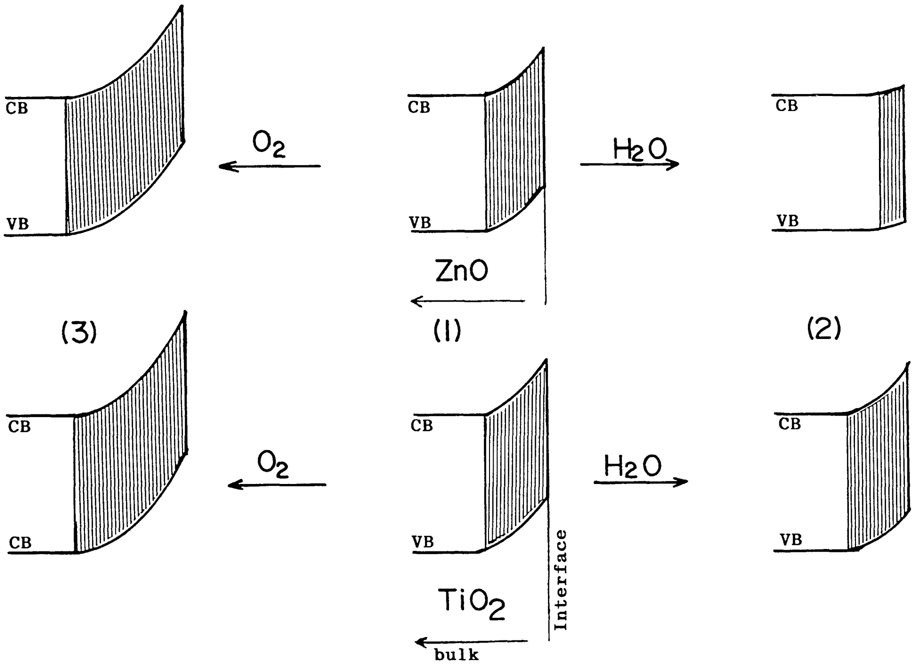

Fig. 9. Schematic description of the surface band bending of ZnO (top) and TiO_2 (bottom). (1): after degassing in vacuo (n-type semiconductors), (2): after adsorption of H_2O (decrease of band bending by formation of positively-charged species on the surfaces), (3) after adsorption of O_2 (increase of band bending by formation of negatively-charged species on the surfaces).

encountered on these catalysts. Much larger differences are observed in the activation of H_2O and/or surface OH groups, while only small differences are observed in reactions associated with the activation of O_2 in dry systems. Thus, the observed large photoreactivity differences between wet TiO_2 and ZnO arise from the much faster recombination of photogenerated electrons and holes on the surface of wet ZnO than that on TiO_2, because the formation of the positively-charged surface adducts from H_2O and/or $CH_3C\equiv CH$ results in much smaller upward band bending on ZnO than on TiO_2. On the other hand, in dry systems, the formation of the negatively-charged surface adducts of O_2 leads to much larger upward band bending on both TiO_2 and ZnO, producing higher photocatalytic efficiencies for TiO_2 and ZnO and negligible differences in their reactivities.

Conclusions

The photocatalytic reactivities of powdered TiO_2 and ZnO, both Pt-loaded and native, differed significantly in the photocatalytic hydrogenation of $CH_3C\equiv CH$ and C_3H_6 with H_2O but not in the photocatalytic oxidation of i-C_4H_8 and C_3H_6 with O_2. Photoluminescence of TiO_2 and ZnO in the presence and the absence of H_2O or O_2 indicated that addition of H_2O onto the oxides causes downward band bending to increase the efficiency of recombination of photogenerated electrons and holes, to a greater extent on ZnO than on TiO_2. On the other hand, the addition of O_2 led to upward band-bending to suppress recombination of photogenerated electrons and holes almost equally on the two oxides.

Thus, photoluminescence of TiO_2 and ZnO (as radiative recombination of photogenerated electrons and holes), together with the direct ESR detection of reaction intermediates, suggested that the large observed difference in the photoreactivity between wet TiO_2 and ZnO derives from the much faster recombination on ZnO because of the formation of positively-charged surface adducts. In dry systems, the formation of the negatively-charged O_2 proceeds nearly equivalently on these two catalysts, resulting in a net higher photocatalytic efficiencies of both TiO_2 and ZnO but little difference in their reactivities.

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