Photocatalytic Hydrogenation of Ethylene on the Bimetal-Deposited Semiconductor Powders

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Abstract: Photocatalytic hydrogenation of ethylene (PHE) was studied on some bimetal-loaded TiO_2 powders and on monometal loaded samples. The metals employed were Pd, Pt, Cu, and Ni. For the selective production of ethane, the combination of Pt and Cu as cocatalysts showed a collective effect in the titled reaction. When the selectivity of produced C_2H_6 to CH_4 was improved by the optimum ratio of Pt to Cu on TiO_2, the volume of the concurrently evolved H_2 was diminished. This suggested that the Pt surface which was spatially controlled with the codeposited Cu afforded a desirable geometry for the photohydrogenation of C_2H_4. A possible reaction mechanism and the advantage of the composite surface of the bimetal-loaded TiO_2 powders are discussed.

In the last decade, more and more studies have been done on photocatalytic reactions using various kinds of semiconductor powders.[1] In most cases, the semiconductor particles were modified with a metal and/or a metal oxide as cocatalyst. Such a cocatalyst was assumed to provide redox sites on the photocatalyst powder; e.g., a deposit of a noble metal makes the cathodic site in the photocatalytic decomposition of water.[2] Noble metals, e.g., Pt, Pd, and Rh, were supposed to be best in the catalytic activity for a variety of photocatalytic reactions, and Pt has been most widely employed as a deposited metal. The noble metal serves as an electron pool to prevent the recombination of photogenerated carriers, and a cathodic reaction, typically hydrogen production, is catalytically promoted on such a metal surface. Aspnes and Heller showed that the microcontact between a loaded metal and a semiconductor particle is nearly ohmic under hydrogen atmosphere.[3] This reasonably supports the idea that the noble metal on powdered semiconductors favors cathodic reactions.

Sakata et al. reported that illuminated TiO_2 powders with only 0.01 monolayer (0.005 mol %) of Pt afforded the maximum evolution rate of hydrogen from water in an ethanolic solution.[4] They also showed that the catalytic activity was maintained even when the Pt amount was as low as 0.001 monolayer. Below this quantity, the catalytic activity decreased rapidly. This implies that the reaction is quite sensitive to both the size and the dispersion of the deposited islands of cocatalyst, because their size varies with the total amount of Pt but the number of the islands does not change much.[5]

When the platinum deposits are too small, for example, the hydrogen atoms produced photocatalytically on them can easily flow over onto the bare surface of TiO_2 and readily react with oxidized intermediates. Thus, hydrogen evolution will be suppressed. Naturally, a close location between the reduction and oxidation sites on a photocatalyst surface can affect both the yield and the reaction products. Unless a given reaction is irreversible, very finely deposited platinum on the semiconductor powders will be deleterious for the photocatalysis, because the more closely spaced the redox sites are, the more easily the back-reaction occurs. In contrast, a close spacing of both sites can be helpful for a coupling reaction of reduced and oxidized forms of short-living intermediates. Thus, the surface design of the photocatalyst particles is important from the viewpoint of developing and controlling photocatalytic reactions.

A combination of cocatalysts, viz., Pt and RuO_2, has been utilized to promote the photocatalytic decomposition of water,[6] though RuO_2 was revealed to act as another reduction site.[7] To the best of our knowledge, however, a composite cocatalyst of two metals has not hitherto been investigated for the surface design of the photocatalyst particles. In this respect, a photocatalytic hydrogenation of ethylene (PHE, eq 1) was examined as a model

$$C_2H_4 \xrightarrow[h\nu, \text{ photocat.}]{H_2O} C_2H_6 \qquad (1)$$
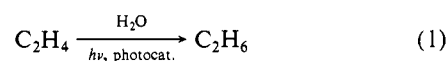
reaction on various bimetal-deposited TiO_2 particles, in order to demonstrate a collective effect of the two metals. The information on such a collective effect will be a clue to understand the mechanisms of photocatalytic reactions more completely.

There have been several studies of the photocatalytic hydrogenation of alkynes and alkenes. Boonstra and Mutsaers[8] reported that the hydrogenation of acetylene and ethylene proceeded on illuminated TiO_2 powders, accompanying the fission of $C\equiv C$ or $C=C$ bond. They suggested that the reaction was caused by hydrogen radicals which were dissociatively produced from the surface hydroxyl groups under near-UV irradiation of TiO_2. Their report was reexamined by Schrauzer and Guth,[9] who concluded that the hydrogenation was brought about by hydrogen atoms produced by the photodecomposition of water molecules adsorbed on the TiO_2 surface. The participation of the photocatalytic decomposition of water in the photohydrogenation of ethylene was also demonstrated by Sato and White, using Pt/TiO_2 powders.[10]

Because deposited Pt is effective for the photocatalytic production of H atoms from water, i.e., from H^+'s (eq 2), it is supposed that Pt/TiO_2 works well for the photohydrogenation of ethylene (eq 3). Anpo et al.[11] argued that the deposited Pt on

$$H^+ + e^- \xrightarrow{Pt} H \qquad (2)$$

$$CH_2=CH_2 + 2H \rightarrow CH_3CH_3 \qquad (3)$$

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2274 *J. Am. Chem. Soc., Vol. 109, No. 8, 1987*

Baba et al.

TiO$_2$ powders contributed to the separation of photoinduced electrons from holes in the photohydrogenation of ethylene without C=C bond fission. Even in their report, however, accumulation of degraded C$_1$ products, such as CH$_4$, CO, and CO$_2$, was observed. Hence, PHE on TiO$_2$ powders modified with a composite cocatalyst was studied in this paper to improve the product selectivity of ethane. The information obtained will be useful for the further understanding of the photocatalytic reactions on semiconductor particles.

Experimental Section

Materials. TiO$_2$ powder was provided by Nihon-Aerosil Co. (P-25: BET surface area is 50 m^2/g, average particle size is 300 Å in diameter) and was used without pretreatment. Metalization was done at the level of 1 wt % of the substrate TiO$_2$ by the photoelectrochemical method that was almost similar to that reported by Bard et al.[12] In the preparation of a bimetal-loaded TiO$_2$ sample, the corresponding metal chlorides were introduced at the same time in an air-tight tube of Pyrex glass. The mixed aqueous suspension, containing TiO$_2$, metal chlorides, and ethanol as a reducing reagent,was deaeriated by the evacuation of the tube, stirring vigorously with a magnetic bar. Then the reaction tube was sealed with a stopcock, and the dispersion was illuminated for several hours with a 500-W high-pressure mercury lamp through a water jacket to cut off the thermal part of the irradiation light. The suspension turned gray (or reddish in case of copper) almost in 1 h. The resultant colored slurry was repeatedly washed with distilled water and was centrifuged. The precipitate was dried overnight in an oven at 80 °C and then was well-crushed to be stored in air. Monometallic copper or nickel was loaded on TiO$_2$ powders in almost the same manner as above, except for rather prolonged illumination. The photocatalysts thus prepared were analyzed qualitatively and quantitatively by means of an EPMA (Xevex MAGIC-5). It was confirmed that each metal was deposited on TiO$_2$ powders and that the proportion of two metals by weight on a bimetallic sample was kept at the original concentration ratio in the solution used in the preparation.

Procedure. A sample catalyst of 0.1 g by weight was spread in the flat bottom reactor which was attached to a closed circular system of 712-mL inner volume. The system was fully evacuated beforehead, and the mixture of water vapor and ethylene was introduced at room temperature. The mixture of the reactant gas was typically at 5 torr with 70 μmol of H$_2$O and 140 μmol of C$_2$H$_4$. The photocatalyst in the reactor was illuminated from beneath with a white light of a 250-W high-pressure mercury lamp (Ushio USH 250D), and the reactant gas was circulated continuously with a magnetically driven pump. A portion of the reaction gas was periodically sampled using a particular port of 1-mL volume. This sampling port was constructed with two stopcocks that connected the closed circular system to a mass analyzer through a conventional vacuum line. The sampled gas was measured quantitatively with a pressure gauge (MKS Baratron 227A) after transfer into the vacuum line and was analyzed with a quadrupole mass filter (Anelva AGA-100). Mass spectra were recorded in the 1–100 amu range. The observed mass spectrum, with background subtracted, was interpreted in terms of the reported cracking pattern coefficients of the referred compounds, as well as of those obtained for standard samples with the present analyzer.

Results and Discussion

Photoinduced Hydrogenation of Ethylene over Bi- and Monometal-Loaded TiO$_2$ Powders. In contrast to the report of Yun et al.,[11,13] the photoproductions of C$_3$H$_8$ and other rearranged hydrocarbons were found substantially below the identification limit in this study. Only CH$_4$ and C$_2$H$_6$ were identified as the photohydrogenated products with all of our prepared photocatalysts. Thus, quantitative discussion is restricted to H$_2$, CH$_4$, C$_2$H$_6$, and CO$_2$, as well as H$_2$O and C$_2$H$_4$.

As reviewed in the introduction, ethylene is photohydrogenated to methane on bare TiO$_2$, and ethane was produced on Pt/TiO$_2$ without the fission of the C=C bond. Figure 1 shows the time course of the photohydrogenation of ethylene on our Pt/TiO$_2$ powders. From this figure, note that the production of C$_2$H$_6$ almost stopped in 2 h, even though ethylene was still left in the
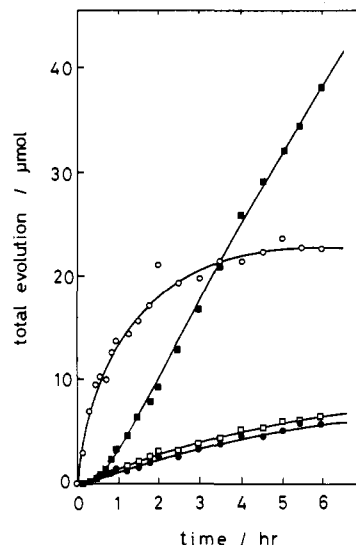
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Figure 1. Time course of the photohydrogenation of ethylene on Pt/TiO$_2$: (O) C$_2$H$_6$, (●) CH$_4$, (□) CO$_2$, and (■) H$_2$. The reactants were introduced at 5 torr with 70 μmol of H$_2$O and 140 μmol of C$_2$H$_4$. The residual C$_2$H$_4$ at 6 h of irradiation was ca. 100 μmol.
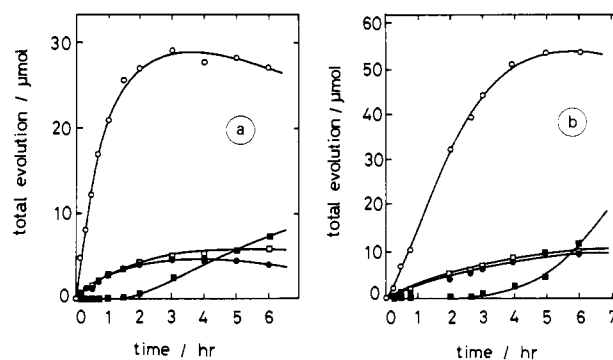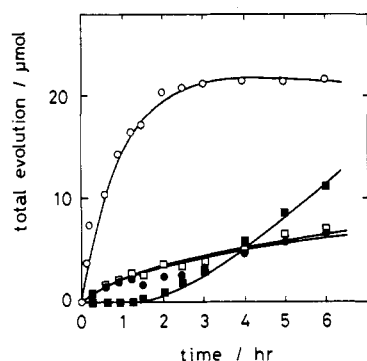

Figure 2. Time course of the photohydrogenation of ethylene on (a) Pd/TiO$_2$ and (b) Pd/TiO$_2$/Ni: (O) C$_2$H$_6$, (●) CH$_4$, (□) CO$_2$, and (■) H$_2$. Reactants were (a) 30 μmol of H$_2$O and 50 μmol of C$_2$H$_4$ and (b) 50 μmol of H$_2$O and 150 μmol of C$_2$H$_4$.

system. In addition, H$_2$ evolved remarkably in contrast to the suppression of C$_2$H$_6$ production. Thus, the adsorption of ethylene molecules on Pt/TiO$_2$ was not supposed to be regenerative under photohydrogenation.

The catalyst modified with Pd and Ni (Pd/TiO$_2$/Ni) was first adopted as the composite photocatalyst to promote the adsorption of ethylene. The result is shown in Figure 2. For Pd/TiO$_2$/Ni, Pd was assumed to supply the reaction with hydrogen atoms from the photocatalytic decomposition of water on its surface, and Ni offered the adsorption site for an ethylene molecule accepting the π-electron of a C=C bond into its vacant d orbital. The time course of the PHE on Pd/TiO$_2$/Ni was apparently similar to that on Pd/TiO$_2$, although the total amount of the products on Pd/TiO$_2$/Ni was twice as much as that on Pd/TiO$_2$ due to the larger quantity of reactants introduced. Thus, the photoproduction of C$_2$H$_6$ on Pd/TiO$_2$/Ni could be largely attributed to the catalytic activity of Pd dispersed on the TiO$_2$ surface, because no C$_2$H$_6$ was observed over the illuminated Ni/TiO$_2$ as shown in Figure 4c.

Pt/TiO$_2$/Cu was prepared as another bimetal-loaded sample. When Pt and Cu were loaded simultaneously, each at 1 wt % of the TiO$_2$ powders, this photocatalyst showed almost the same activity in the photoproduction of ethane as Pt/TiO$_2$ (Figure 3), whereas the hydrogen evolution rate of Pt/TiO$_2$/Cu was almost half as fast as that of Pt/TiO$_2$ (Figure 1 and 3). We suggest that in PHE on a composite surface, like Pt/TiO$_2$/Cu, the rate of hydrogen evolution is reduced by the codeposition of Cu and Pt without the suppression of ethane formation. Since H$_2$ was evolved through the photocatalytic decomposition of adsorbed water, this result suggested an effective supply of hydrogen atoms to ethylene

Photocatalytic Hydrogenation of Ethylene

J. Am. Chem. Soc., Vol. 109, No. 8, 1987 2275

Figure 3. Time course of the photohydrogenation of ethylene on Pt/TiO$_2$/Cu: (O) C$_2$H$_6$, (●) CH$_4$, (□) CO$_2$, and (■) H$_2$. The reactants were introduced at 5 torr with 70 μmol of H$_2$O and 140 μmol of C$_2$H$_4$.

Figure 4. Time courses of the photohydrogenation of ethylene on (a) Cu/TiO$_2$/Ni, (b) Cu/TiO$_2$, and (c) Ni/TiO$_2$; (O) C$_2$H$_6$, (●) CH$_4$, (□) CO$_2$, and (■) H$_2$. Reactants were (a) 50 μmol of H$_2$O and 100 μmol of C$_2$H$_4$, (b) 40 μmol of H$_2$O and 80 μmol of C$_2$H$_4$, and (c) 20 μmol of H$_2$O and 40 μmol of C$_2$H$_4$.

Figure 5. Dark hydrogenation of ethylene on the composite photocatalysts at room temperature. The 1:1 mixture gas of C$_2$H$_4$ + H$_2$ was introduced over 0.1 g of each catalysts: (a) Pd/TiO$_2$, reactant gas = 1 torr, (b) Cu/TiO$_2$/Ni, reactant gas = 10 torr, and (c) Pt/TiO$_2$/Cu, reactant gas = 1 torr.

molecules on the surface of Pt/TiO$_2$/Cu.

When Cu/TiO$_2$ or Ni/TiO$_2$ was used as a photocatalyst in PHE, no C$_2$H$_6$ was observed (Figure 4). Hydrogen was evolved more in the case of Cu/TiO$_2$ than in the case of Ni/TiO$_2$, while CO$_2$ and CH$_4$ were observed in both cases. Naturally, the combination of Cu and Ni exhibited no collective effect on the photoproduction of ethane (Figure 4).

As seen in Figure 1, the initial rate of C$_2$H$_6$ production was comparatively fast on Pt/TiO$_2$, and at the same time H$_2$ evolution was almost suppressed. After 1 h of irradiation, H$_2$ was evolved remarkably and the C$_2$H$_6$ formation was rapidly degraded. This suggested that the reaction sites which were once covered with hydrogen atoms were scarcely accessible for ethylene molecules. Therefore, for the sustained photohydrogenation of ethylene, the site for ethylene adsorption should be located in the vicinity of the site for the photocatalytic production of hydrogen atoms. One of the ways possible is to disperse such a metal on the photocatalyst surface that preferentially adsorbs ethylene molecules instead of hydrogen atoms. Thus, a better catalyst for PHE can be realized by the codeposition of the two metals on powdered semiconductors: one, for example, a platinum group metal, promotes the photocatalytic production of hydrogen atoms from water; the other facilitates the ethylene adsorption on the catalyst surface.

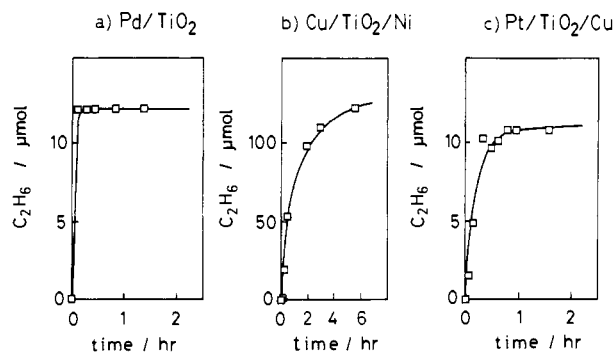The hydrogenation of ethylene in the dark was catalyzed on alloys such as Cu/Ni[14] and Pd/Ni[15] when a mixture of C$_2$H$_4$ and

H$_2$ was introduced over them. In addition, catalytic hydrogenation of ethylene in the dark was demonstrated on our composite photocatalysts under a C$_2$H$_4$ + H$_2$ atmosphere at room temperature (Figure 5). Cu/TiO$_2$/Ni was successful in the dark hydrogenation of ethylene but failed in PHE for C$_2$H$_6$ production.

It is generally assumed that a transition-metal catalyst enhances adsorption of reactants by accepting their electrons into its inner incomplete d orbital. The d orbital of a given transition metal can be partially occupied with an outer-shell s electron of another metal when they are alloyed. This alloy is supposed to exert a controlled adsorption of reactants and a smooth desorption of products. Hence, a pair of metals, one of which must be a noble metal, is recommended as a composite cocatalyst for PHE. Here, the other metal should work in either way: to adsorb an ethylene molecule on its surface or to modify dimensionally the noble metal surface to make it more suitable for ethylene adsorption. If the former is the case, the metal should not adsorb hydrogen atoms too strongly. From this point of view, Pt/TiO$_2$/Cu is one candidate for PHE, because Cu can hardly chemisorb hydrogen.[16]

From Figure 1, Pt/TiO$_2$ seems unsatisfactory for PHE, because CH$_4$ and CO$_2$ were produced in an appreciable amount. The production of CH$_4$ and CO$_2$ was brought about by the rupture of the C=C bond of ethylene, and this double bond fission was supposed to be caused by hydrogenolysis on the Pt surface or by attack with O$^-$ produced on the TiO$_2$ surface.[13,17] The fission could also be due to the direct scavenging of h$^+$ on the bare TiO$_2$ surface by the π-electron of the ethylene C=C bond. Thus, if only an adsorption site for ethylene was established on the supported metal surface, degradation of ethylene could be minimized.

Photohydrogenation of Ethylene on Pt/TiO$_2$/Cu. To elucidate the active roles of the supported metals in PHE, especially Cu as an "assistant" metal, a series of experiments on the photohydrogenation of ethylene with the Pt–Cu codeposited TiO$_2$ catalysts were carried out. Those photocatalysts used with 1-Pt/0.2-Cu, 1-Pt/1-Cu, 1-Pt/2-Cu, and 2-Pt/2-Cu, where the numbers in these abbreviations represent the loaded amount of the corresponding metals in units of wt % of the substrate TiO$_2$ powders.

Figure 6 shows the variation in the time course of the photohydrogenation of ethylene on 1-Pt/0.2-Cu, 1-Pt/1-Cu, and 1-Pt/2-Cu. The time profiles of the photoproduction of CH$_4$ and CO$_2$ appeared almost the same in all experiments with different catalysts. As seen in Figure 6, a Cu content of 1 wt % leads to greater production of C$_2$H$_6$ and to smaller evolution of H$_2$ at the same time. Since the catalysts used differ from each other only in the amount of loaded copper, this figure indicates that there

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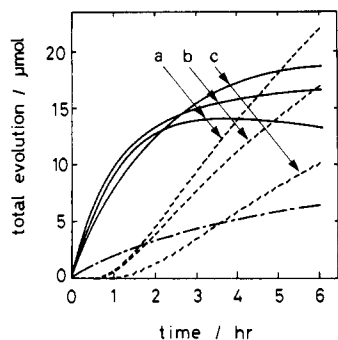(17) Anpo, M.; Aikawa, N.; Kubokawa, Y. *J. Phys. Chem.* **1984**, *88*, 3998–4000.

2276 *J. Am. Chem. Soc., Vol. 109, No. 8, 1987*

Baba et al.

Figure 6. Time courses of the photohydrogenation of ethylene on (a) 1-Pt/2-Cu, (b) 1-Pt/0.2-Cu, and (c) 1-Pt/1-Cu. The time profile of the photoproduction of both CH_4 and CO_2 (dashed–dotted line) appeared almost the same in the case of each catalyst. Reactants were introduced at 5 torr for each experiment (70 μmol of H_2O + 140 μmol of C_2H_4). Solid lines and dotted lines represent those time profiles of C_2H_6 and H_2, respectively.
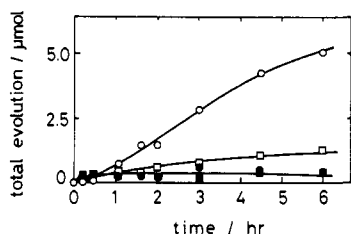

Figure 7. Time course of the photohydrogenation of ethylene on 2-Pt/2-Cu: (O) C_2H_6, (●) CH_4, (□) CO_2, and (■) H_2. Reactants were 20 μmol of H_2O and 40 μmol of C_2H_4.

was a optimal amount of loaded Cu with Pt for the efficient production of C_2H_6 in PHE. For the clarity of the PHE efficiency, the amount of the effectual hydrogen atoms was tentatively estimated for each catalyst after 6 h of illumination. Here we define an effectual hydrogen ratio (R_{eff}) as

$$R_{eff} = a(C_2H_6)/[a(H_2) + a(C_2H_6)] \qquad (4)$$

where $a(C_2H_6)$ represents the amount of H atoms incorporated in the produced C_2H_6 (i.e., two H's for one C_2H_6) and $a(H_2)$ is that in the evolved H_2. As a result, the R_{eff}'s were 0.37, 0.48, and 0.65 for 1-Pt/2-Cu, 1-Pt/0.2-Cu, and 1-Pt/1-Cu, respectively.

As far as R_{eff}'s were concerned, the 1-Pt/1-Cu sample seemed to be best among the three. Subsequently, a 2-Pt/2-Cu sample was examined to find how a large quantity of the metals works in PHE. The result is shown in Figure 7. Though the catalytic activity of 2-Pt/2-Cu was low, the longer the catalyst was irradiated, the better was both the R_{eff} and the selectivity of produced ethane from methane. It can also be emphasized that the production of free H_2 was almost suppressed except in the early stage and that the photohydrogenation proceeded selectively to C_2H_6 under prolonged irradiation. The R_{eff} of 2-Pt/2-Cu was as high as 0.94 after 6 h of irradiation (Figure 8).

There were still two problems left to be elucidated: the one in the reaction mechanism of PHE and the other in the role of Cu. It is necessary for efficient PHE that the fission of the C=C bond should be minimized and that the adsorption of ethylene on the catalyst surface should be promoted.

On the former subject, Anpo et al. argued that a localized O^-–h^+ center, i.e., Ti^{3+}–O^-, which was produced on the surface of bare TiO_2 under the band-gap illumination, broke the ethylene C=C bond.[11,13,18] They suggested that platinized TiO_2 particles afforded separate sites for photogenerated electrons and holes, which brought about the hydrogenation of ethylene without the C=C cleavage.[17] The generation of CH_4 and CO_2, observed even on Pt/TiO_2, was also explained to be due to the attack by O^- or $^\bullet OH$
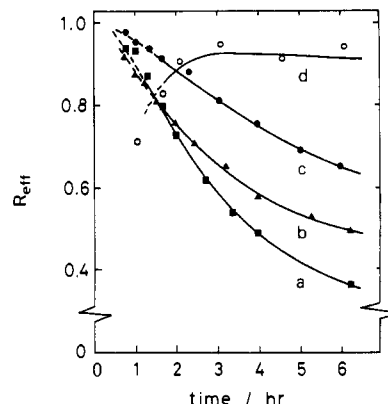

Figure 8. Time dependence of R_{eff}'s on (a, ■) 1-Pt/2-Cu, (b, ▲) 1-Pt/0.2-Cu, (c, ●) 1-Pt/1-Cu, and (d, O) 2-Pt/2-Cu. R_{eff}'s were calculated from those data of Figures 6 and 7.

radical which was formed with h^+ and OH^-. In the case of 2-Pt/2-Cu, however, the C_1 products were less in quantity, while C_2H_6 was steadily evolved. This is probably because the larger amount of the metals on the catalyst surface prevented incident light from yielding a high surface density of O^- or $^\bullet OH$. Thus, the fission of the C=C bond on 1-Pt/1-Cu is expected to be minimized under a moderate illumination.

As for the latter requirement, ethylene was reported to be adsorbed on the metallic copper with a surface coverage of several percent at room temperature.[19] Ni should also adsorb ethylene to some extent because of its vacant 3d orbital. When Cu/TiO_2 was compared with Ni/TiO_2 in the PHE behavior, the difference in the hydrogen evolution rates corresponded to that in the ethylene coverage on each loaded metal. The lack of C_2H_6 photoproduction on both catalysts suggested difficulties in supplying hydrogen atoms available for PHE, because of the lower surface coverage either of ethylene on Cu or of hydrogen on Ni. Therefore, the deposited copper of $Pt/TiO_2/Cu$ functions as an assistant metal in PHE to promote ethylene adsorption on Pt. Furuya et al. reported that Cu adatoms at a particular surface coverage on a Pt electrode promoted the adsorption of C_2H_4 and thus showed efficient electrochemical hydrogenation of ethylene on such an electrode.[20] Hence, the function of the codeposited Cu in the case of $Pt/TiO_2/Cu$ can be regarded as almost similar to that of Cu adatoms.

To understand the catalytic nature of $Pt/TiO_2/Cu$, information about the surface morphology of the catalyst is quite significant.[21] Upon simple calculation, the surface coverage by the platinum deposits at 1 wt % of TiO_2 was estimated as at most 20% of a monolayer, while that of copper in the same amount corresponded to about 3 times that of Pt. This is, of course, untrue for the actual surface, since metals are supposed to be deposited in the form of scattered islands.[5] An attempt to observe the catalyst surface failed to disclose the morphology of the metal islands employed, by the use of either a scanning electron microscope even at the magnification of ×50000 or by an EPMA in the spot analysis mode. This was because the deposited metal islands were too fine to be probed with the electron beam employed.

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(21) According to Burton and Garten (*Advanced Materials in Catalysis*; Academic: New York, 1977), the synergic behavior of the bimetallic cluster catalyst was interpreted in terms of an ensemble effect and a ligand effect.

(22) Somorjai et al. proposed a new mechanism for the catalytic hydrogenation of ethylene in terms of ethylidyne (*J. Am. Chem. Soc.* **1984**, *106*, 2288–2293), rather than the associative mechanism of Horiuti and Polanyi (*Trans. Faraday Soc.* **1934**, *30*, 1164–1172) and the dissociative mechanism of Farkas and Farkas (*J. Am. Chem. Soc.* **1938**, *60*, 22). Very recently, however, the direct involvement of ethylidyne in the catalytic hydrogenation of ethylene has been modified by Beebe et al. on Pd/Al_2O_3 (*J. Am. Chem. Soc.* **1986**, *108*, 663–671). Somorjai et al. also suggested (*J. Am. Chem. Soc.* **1985**, *107*, 5910–5920) that the electrochemical hydrogenation of ethylene in aqueous solution proceeds by the scheme identical with that postulated by Horiuti and Polanyi.

The reaction mechanism of PHE on Pt/TiO$_2$/Cu and the exact location of the reaction sites are still ambiguous, even when considering those proposed for the catalytic hydrogenation of ethylene.[22] A collective effect of Pt and Cu codeposited on TiO$_2$ particles was observed in the selective production of C$_2$H$_6$ in PHE, i.e., the hydrogenation of ethylene assisted by the photocatalytic production of hydrogen atoms from water. A further study in the collective effect of Pt/TiO$_2$/Cu on PHE is now under way.

Heteronuclear NMR Studies of Cobalamins. 6. The Nucleotide Loop of Base-Off Cobalamins and the Nature of the Base-Off Species[1]

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Abstract: The acid–base properties of α-ribazole-3′-phosphate, the detached axial nucleotide of cobalamins, have been studied by potentiometric and spectrophotometric techniques at 25.0 ± 0.1 °C, ionic strength 1.0 M. The microscopic pK_a for proton dissociation from the benzimidazolium moiety of the zwitterion (relevant to the base-on/base-off protonic equilibrium of cobalamins) is 5.54 and the isoelectronic point 2.94. The ^{13}C NMR resonances of the nucleotide loop carbons of a series of five protonated, base-off alkylcobalamins have been directly compared with those of the zwitterion of the free nucleotide in order to detect any noncovalent interactions between the pendent, protonated axial nucleotide and the remainder of the structure in the base-off forms. The comparison shows no significant differences along the top of the benzimidazole moiety (B9, B4, B10) or at R1 or R5, but significant differences at B5, B6, B7, B8, R2, R3, and R4. Considering the available X-ray structures of base-on cobalamins, these chemical shift perturbations do not readily suggest an interaction between the pendent nucleotide and the remainder of the structure. A similar comparison between the nucleotide loop ^{13}C resonances of two base-off, but benzimidazole deprotonated, alkyl(cyano)cobalamins and the dianion of the free nucleotide shows significant chemical shift perturbations at all benzimidazole carbons except B7, strongly suggesting an interaction between the pendent, but benzimidazole deprotonated, nucleotide and the remainder of the structure in the deprotonated base-off forms. A comparison between the ^{13}C NMR spectrum of base-off dicyanocobalamin and dicyanocobinamide (from which the axial nucleotide has been removed) suggests that the major interaction is formation of a hydrogen bond between the benzimidazole nitrogen (B3) and an amide hydrogen on the e propionamide side chain.

One of the most characteristic and perhaps one of the most thoroughly studied chemical properties of cobalamins is the so-called base-on/base-off reaction in which the axially coordinated dimethylbenzimidazole nucleotide is displaced by water and protonated (eq 1). This reaction is sometimes referred to as the

(1)
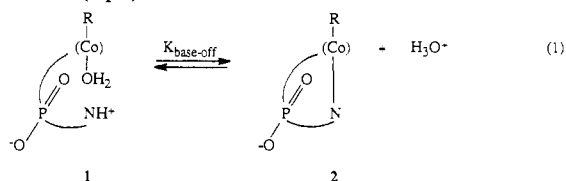
"red-yellow" shift due to the large changes in electronic spectrum attendant upon conversion of the base-on (**2**) to the base-off (**1**) form.[2] Many values of p$K_{base-off}$ (eq 1) have been determined (generally spectrophotometrically) and large tabulations of such values exist.[3] This protonic equilibrium is often conveniently viewed as the sum of two consecutive equilibria (eq 2 and 3)[1,4–14]

(2)

(3)
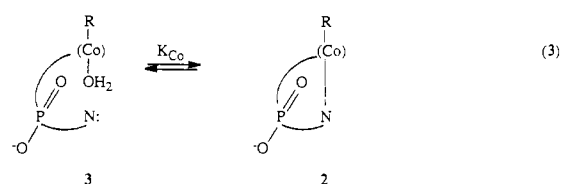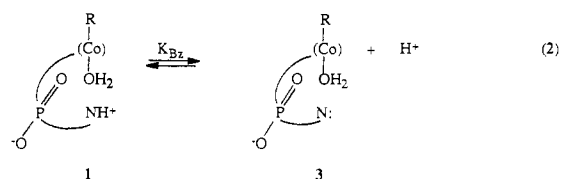
for which eq 4 relates the value of $K_{base-off}$ (eq 1) to the equilibrium

$$K_{base-off} = (1 + K_{Co})K_{Bz} \qquad (4)$$

constants of eq 2 and 3. It is then often assumed that K_{Bz} (eq 2) is equivalent to the pK_a of the conjugate acid of the detached axial nucleoside (i.e., 1-α-D-ribofuranosyl-5,6-dimethylbenz-

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