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Photocatalytic Isomerization of 1-Butene over Palladium-Loaded Titanium(IV) Oxide Particles: Lewis Acid-like Features of the Photocatalyst

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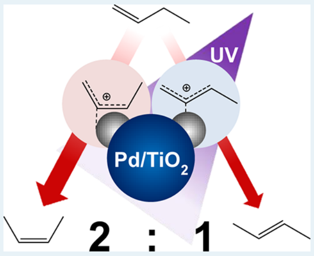
ABSTRACT: 1-Butene was isomerized to 2-butenes with a cis:trans ratio of ~2:1 over Pd/TiO_2 under irradiation of UV light at room temperature, suggesting that a Pd/TiO_2 photocatalyst can function as an effective substitute for a Lewis acid catalyst and that the reaction rate can be controlled by photon flux as in the case of changing temperature in a thermocatalytic system.



KEYWORDS: *photocatalyst, isomerization, 1-butene, TiO_2, palladium*

1. INTRODUCTION

Acid–base catalysts have been developed or improved because they are often used in syntheses of industrially important chemicals.[1−4] To achieve a clean process in organic syntheses, precise control of the acidity, basicity, or their site number of the catalysts during the reaction is important. Acid and base are defined in terms of electron transfer by Lewis as follows: electron acceptor and donor are acid and base, respectively. When semiconductor photocatalysts, such as titanium(IV) oxide (TiO_2), are irradiated by UV light, charge separation occurs, and electrons in the conduction band and holes in the valence band cause reduction and oxidation, respectively. In addition, these electrons and holes act as electron donors and acceptors, respectively. A semiconductor photocatalyst might hence be useful for syntheses of industrially important chemicals as a conventional substitute of an acid–base catalyst. Moreover, the amount of electrons and holes excited by photons linearly depends on light intensity (amount of photons provided). Though the activity of solid acid–base catalysts generally decreases in the presence of water, photocatalysts are often water-resistant. In fact, a photocatalytic reaction proceeds at room temperature and under atmospheric pressure even in the presence of water. Since a photocatalytic reaction satisfies almost all of the 12 proposed requirements for green chemistry, organic synthesis of various compounds using photocatalysts has been studied by many researchers.[5−15] We have studied application of a TiO_2 photocatalyst for reduction of nitro aromatics to corresponding amino aromatics.[16,17] We also found that Tishchenko reaction occurred via dimerization of formaldehyde in the photocatalytic oxidation of methanol over TiO_2 with oxygen to methyl formate.[18] Since Tishchenko reaction involves a step reaction by Lewis acid, the results lead to the idea that a TiO_2 photocatalyst can be useful for syntheses as a substitute catalyst for Lewis acid; its acidity or the number of acid sites can be controlled by light intensity (amount of photons). To clarify the characters of the acid–base catalysts, the relations between formation ratio of the geometrical isomers and acidic properties of the catalysts have been studied in detail in the thermal isomerization of alkenes. There have already been some studies on the activity of photocatalysts such as TiO_2 and CdS in the geometrical cis–trans isomerization of butene.[19−21] However, those catalysts were less active and those studies were not carried out from the point of view of an acid–base catalyst. There have been few studies on acidic behaviors of photocatalysts under irradiation of UV light. Therefore, we studied the acidic behaviors of TiO_2, which is one of the most important photocatalysts, under irradiation of UV light. We found that the photocatalytic isomerization of 1-butene to 2-butenes occurred over TiO_2 and palladium-loaded TiO_2 (Pd/TiO_2). In this paper, we report (1) higher activity of Pd/TiO_2 for the isomerization, (2) Lewis acid-like features of the Pd/TiO_2 photocatalyst, and (3) controllable activity with light intensity.

2. EXPERIMENTAL SECTION

2.1. Reagents. The reactant gases (1-butene (7.1%), *cis*-2-butene (4.0%), and *trans*-2-butene (6.8%)) were of commercial grade (all for nitrogen balance) and used without further purification. Main impurities were butene isomer and butane. Nitrogen gas (>99.99%) was used as inactive gas in the reaction atmosphere. Anatase-type titanium(IV) oxide (TiO_2) powder (ST-01, BET surface area: 300 m^2 g^{-1}) was supplied from Ishihara Industry, Co.

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2.2. Preparation of Pd/TiO$_2$. Palladium(II) acetate (Pd(OAc)$_2$) was dissolved in a small amount of acetic acid solution. The solution was diluted to desired concentrations and used for photodeposition of Pd metal on the surface of TiO$_2$. Anatase-type TiO$_2$ powder was suspended in aqueous solutions of Pd(OAc)$_2$ containing a small amount of acetic acid in a Pyrex test tube, the amount of which corresponded to 0.05, 0.10, 0.20, 0.25, 0.30, 0.50, 1.0, and 2.0 wt. % modification as Pd metal. The test tube was sealed with a rubber septum under argon and then photoirradiated for 3 h at a wavelength $\lambda > 300$ nm by a 400 W high-pressure mercury arc. In the process, acetic acid worked as hole scavenger (reducing agent) and palladium ions in the suspended mixture were photocatalytically reduced on the surface of TiO$_2$, resulting in the formation of Pd/TiO$_2$. The resulting powder was separated with a membrane filter (maximum diameter = 0.1 μm) and dried in vacuo for 1 h in a drying apparatus. The catalysts were stored in sample bottles. Other metals, copper (Cu, chloride), ruthenium (Ru, chloride), rhodium (Rh, chloride), silver (Ag, sulfate), iridium (Ir, chloride), platinum (Pt, hexachloroplatinic acid), and gold (Au, tetrachloroauric acid) were also loaded on the surface of TiO$_2$ by the photodeposition method using the starting materials shown in parentheses in the presence of oxalic acid as hole scavenger.

2.3. Photocatalytic Isomerization. In a typical run, 0.50 wt. % Pd/TiO$_2$ powder (5.0 mg) was homogeneously loaded on a planar glass filter (size = 1 × 3 cm), and the glass filter with Pd/TiO$_2$ powder was placed in a 13 cm^3 Pyrex bottle. Air in the reaction bottle was replaced with nitrogen gas, and the reaction bottle was immediately sealed by a stopper equipped with a rubber sampler. By using a gas syringe, 1-butene (10.0 cm^3) was injected from the rubber sampler into the reaction bottle. UV light (0.87 mW cm^{-2}, < 420 nm) was irradiated to the reaction bottle for a desired period at room temperature using two black lights (Hitachi FL10BL 10W). In some experiments, a blue and red light-emitting diodes (HDMS8B and HDMS8R, Hayashi Watch Works, Tokyo, maximum energy at 457 and 648 nm, respectively, and designated blue and red LED hereafter, respectively) were used to examine effects of wavelength of light. Sampling of the reaction gas was carried out at 5-min intervals. The amounts of formed isomers in the sampling gas were determined by GC with a Unicarbon A-400 column.

2.4. FTIR Measurement. The Pd/TiO$_2$ pellet sample was placed in a Pyrex IR cell with NaCl windows connected to a vacuum line. 1-Butene gas was introduced under the pressure of 5 kPa into the cell after pretreatment in vacuo at room temperature for 2 h. Irradiation of the pellet samples was carried out using black light (Hitachi FL10BL, 10W) prior to FTIR measurements. FTIR spectra were measured at room temperature using a Shimadzu FTIR spectrometer (FTIR-8300).

2.5. Diffuse Reflectance Spectra and Action Spectrum Analysis. Diffuse reflectance spectra of Pd/TiO$_2$ samples were obtained with a UV−visible spectrometer (UV-2400, Shimadzu, Kyoto) equipped with a diffuse reflectance measurement unit (ISR-2000, Shimadzu), in which barium sulfate was used as a reference sample. To obtain an action spectrum, the full arc from the Xe lamp was monochromated with light width of ±5 nm using SM-100 (Bunkoukeiki, Tokyo). Light intensities were determined using a spectroradiometer USR-45D (Ushio, Tokyo). Assuming that one photon is required for formation of one product, apparent quantum efficiency (AQE) at each centered wavelength of light was calculated from the ratio of the amount of 2-butenes and the amount of photons irradiated using the following equation:

$$\mathrm{AQE} = \frac{\text{amount of formed 2-butenes}}{\text{amount of incident photons}} \times 100$$

3. RESULTS AND DISCUSSION

3.1. Photocatalytic Double-Bond-Shift Isomerization of 1-Butene over Pd/TiO$_2$. Photocatalytic double-bond-shift isomerization of 1-butene over 0.50 wt. % Pd/TiO$_2$ was studied at room temperature in the dark and under irradiation of UV light. Time courses of the amount of butene isomers over 0.50 wt. % Pd/TiO$_2$ are shown in Figure 1. No isomerization occurred in the dark (even at 343 K) in the absence of hydrogen and under irradiation of visible light, whereas 1-butene transformed to *trans*- and *cis*-2-butenes under irradiation of UV light. Photocatalytic hydrogenation of 1-butene (formation of butane) scarcely occurred under UV irradiation, and no hydrogenation proceeded in the dark. The material valance was almost 100% both under light irradiation (UV and visible) and in the dark. These results indicate that only irradiation of UV light induces double-bond-shift isomerization of 1-butene at room temperature under the pressure of 5 kPa and that hydrogenation and polymerization scarcely occur under the same conditions. In addition, isomerization of 1-butene over bare TiO$_2$ occurred very slowly with only about 4 mol % of conversion after 72 h; the rate was determined to be 0.68 nmol s^{-1} g-cat^{-1}. The very small rate of isomerization was nearly equal to that (0.3 nmol s^{-1} g-cat^{-1}) reported for bare P-25 TiO$_2$ by Anpo et al.[20] Isomerization was drastically accelerated by a slight loading of palladium, and the rate over 0.50 wt. % Pd/TiO$_2$, 5.4 μmol s^{-1} g-cat^{-1}, was 8000-times larger than that over bare TiO$_2$ (discussed later). All isomerization rates in these studies were determined from a steady rate at 5 min, because the rates were uneven in initial reaction time. These results lead to the conclusion that a transformation of 1-butene adsorbed on palladium was involved in the photocatalytic double-bond-shift isomerization of 1-butene and that the loading of palladium particles significantly enhanced the isomerization.

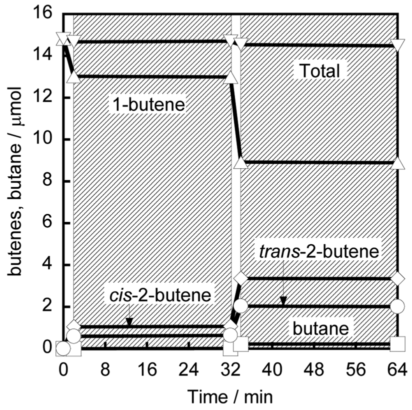

Figure 1. Time courses of the amount of butene isomers over 0.50 wt. % Pd/TiO$_2$. Irradiation of UV light was performed only during the time shown in white and the slanting line indicates the reaction system in the dark.

3.2. FTIR Measurements. An FTIR spectrum for 1-butene adsorbed on 0.25 wt. % Pd/TiO_2 was measured at room temperature under a 1-butene pressure of 5 kPa and is shown in Figure 2. Bands at 2962, 2924, 2908, and 2856 cm^{-1} appeared upon exposure to 1-butene. The spectrum patterns were scarcely changed by UV irradiation. In the literature,[37−39] the adsorption species of 1-butene on noble metals were characterized by IR peaks corresponding to stretching and deformation modes of the ethyl group, at $\nu_{as}(CH_3)$ = 2958 cm^{-1}, $\nu_{as}(CH_2)_{Et}$ = 2931 cm^{-1}, and $\nu_s(CH_3)$ = 2872 cm^{-1}. Furthermore, *cis*-2-butene adsorbed on palladium loaded on metal oxides was characterized by IR peaks for symmetric C−H stretching of terminal methyl groups ($\nu_s(CH_3)$, at 2860 cm^{-1}) and for the fundamental and first overtone mode of asymmetric deformation of terminal methyl moieties ($\delta_{as}(CH_3)$, at 2907 cm^{-1}), whereas the adsorption species of *trans*-2-butene were characterized by IR peaks for asymmetric C−H stretching ($\nu_{as}(CH_3)$, at 2956 and 2937 cm^{-1}) and for the fundamental and first overtone mode ($\delta_{as}(CH_3)$, 2907 cm^{-1}). The frequencies of these modes ($\nu_{as}(CH_3)$) are close to those observed for *trans*-2-butene in the gas phase. Since no *cis*- or *trans*-2-butene wes detected in the dark gas phase by GC analyses, the observed bands at 2962 and 2924 cm^{-1} are attributable to asymmetric stretching ($\nu_{as}(CH_3)$ and $\nu_{as}(CH_2)_{Et}$) of the ethyl group in the 1-butene adsorbed on palladium. Since *cis*-2-butene and *trans*-2-butene are absent in the gas phase, the bands at 2856 and 2908 cm^{-1} are probably attributable to symmetric C−H stretching ($\nu_s(CH_3)$) and the fundamental and first overtone mode ($\delta_{as}(CH_3)$) of asymmetric C−H stretching in the terminal methyl group of a di-σ bonded adsorption species on the palladium surface: butenylcarbenium ion is adsorbed in the dark on the Pd surface by a di-σ-bonding. The band assigned to C═C stretching (ν(C═C) at 1600 cm^{-1}) may be relatively weak and obscure, since the C═C double bond does not undergo strong sp^3-rehybridization because of formation of a di-σ-bonded complex typically seen for alkenes on a metal surface. The IR spectrum supports the idea that 1-butene adsorbs on the palladium metal surface in the dark as a butenylcarbenium ion.

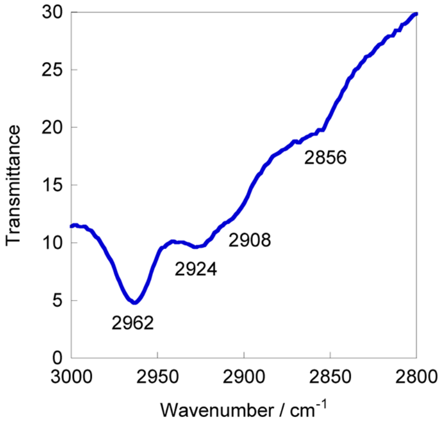

Figure 2. FTIR spectrum for 1-butene adsorbed on 0.25 wt. % Pd/TiO_2 measured at room temperature under a 1-butene pressure of 5 kPa.

3.3. Effect of Metals Loaded on TiO_2. Photocatalytic isomerization over TiO_2 having various metals was examined under the same conditions, and the results are shown in Table 1.

Table 1. Photocatalytic Conversion of 1-Butene over TiO_2 and Metal-Loaded TiO_2 under UV Irradiation[a]

	yield[c] (%)		
metals[b]	butane	*cis*-2-butene	*trans*-2-butene
none	NG	NG	0.30
Cu	NG	0.33	1.6
Ru	NG	NG	NG
Rh	5.0	2.4	2.0
Pd[d]	1.6	23	14
Ag	NG	NG	NG
Ir	0.53	NG	NG
Pt	6.7	0.29	0.34
Au	NG	NG	NG

[a]1-Butene: 24 μmol. Photocatalyst: 5.0 mg. UV intensity: 0.87 mW cm^{-2}. Wavelength λ < 420 nm. Reaction temperature: 297 K. Photoirradiation time: 10 min. [b]Metal: 0.1 wt. %. [c]NG: Negligible. [d]Palladium: 0.5 wt. %. Photoirradiation time: 4 min.

A very small amount of products was observed in the case of copper, rhodium, iridium, and platinum, whereas ruthenium, silver, and gold showed no effect for conversion of 1-butene under the present conditions, suggesting that properties of metals loaded on TiO_2 control isomerization of 1-butene (discussed later).

3.4. Action Spectrum. An action spectrum is a strong tool for determining whether a reaction observed occurs via a photoinduced process or a thermocatalytic process. Action spectrum analysis was carried out at 298 K under irradiation of monochromated visible light from a Xe lamp with light width of ±5 nm, and results are shown in Figure 3.

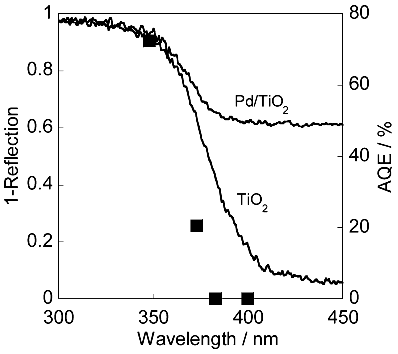

Figure 3. Absorption spectra of TiO_2 and 0.25 wt. % Pd/TiO_2 and action spectrum in isomerization of 1-butene over 0.25 wt. % Pd/TiO_2.

The change in AQE was in agreement with the absorption spectrum of TiO_2. Absorption below 380 nm reflects the band gap of TiO_2 (3.2 eV). Weak absorption at >400 nm was attributable to the impurity level in the conduction or valence bands of TiO_2. Though the color of Pd/TiO_2 was gray and Pd/TiO_2 absorbed visible light, this was due to Pd particles loaded on TiO_2 and no photocatalytic isomerization occurred in the range at >400 nm. These results indicate that the photocatalytic isomerization involved a photoinduced process by the TiO_2 semiconductor, that is, photoexcited electrons in the conduction band of TiO_2 transferred to Pd particles and then contributed to the photocatalytic isomerization. We noted that the value of AQE was quite large (73% at 348 nm). Since the values of AQE in ordinary photocatalytic redox reactions are not so large, the extraordinary value of AQE suggests that photocatalytic double-bond-shift isomerization of 1-butene over Pd/TiO_2 proceeded through a process different from that generally accepted in ordinary photocatalytic redox reactions (discussed later).

3.5. Effects of Intensity of Light. The effects of intensities of UV light and visible light on the rate of isomerization of 1-butene were examined to reveal how the active sites were affected by the amount of incident photons and the results are shown in Figure 4. The rate of isomerization of 1-butene over Pd/TiO_2 was proportional to the intensity of UV light. The light dependency supports the idea that the turnover number of active sites for the isomerization increased with an increase in the number of incident photons, that is, the turnover number of the active sites on Pd/TiO_2 can be controlled by incident photons and the activity of Pd/TiO_2 can be easily quenched by turning the UV light off. In contrast to the results under UV light irradiation, no isomerization of 1-butene occurred under irradiation of visible light from blue and red LEDs. Distributions of light intensity are shown in Figure 5.

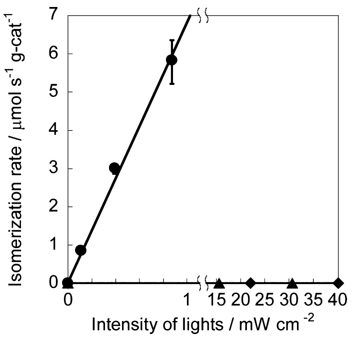

Figure 4. Effects of intensity of UV light (circles) and visible light from blue and red LED (457 and 648 nm, triangles and diamonds, respectively) on isomerization rate over 0.25 wt. % Pd/TiO_2.

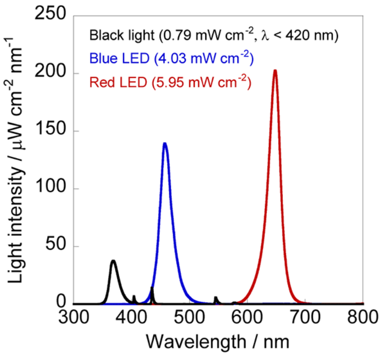

Figure 5. Distributions of intensity of light emitted from black light, blue LED, and red LED.

These results indicate that visible light emitted from the LED did not cause band gap excitation of the TiO_2 photocatalyst. As shown in Figure 4, the intensities of blue light and red light irradiated to the Pd/TiO_2 catalyst were 140−360-times larger than that of UV light (0.11 mW cm^{-2}), indicating that the energies supplied to the catalyst were also 140−360-times larger than that of UV light, that is, the temperature of the catalyst under visible light irradiation must be much higher than that of the catalyst under UV light irradiation because the temperature of the catalyst is connected with the quotient of the supplied energy by its specific heat. If thermal activation of the Pd/TiO_2 catalyst by light irradiated is the key process in the present reaction system, the isomerization of 1-butene should occur under irradiation of intense visible light. However, this was not the case.

3.6. Effect of the Amount of Pd. Effects of the amounts of loaded Pd on the rate of isomerization of 1-butene to 2-butenes were studied, and the results are shown in Figure 6. The rate of isomerization increased linearly with an increase in the amount of loaded Pd up to 0.25 wt. %, and the activity was maintained over the range of 0.25−0.50 wt. %. The activity decreased at more than 0.50 wt. %. The linear increase suggests that the loaded Pd particles dispersed finely on the surface of TiO_2 with maintenance of their electron structure up to 0.25 wt. %. It is known that metals, impurities or defects usually induce an increase in recombination of excited electrons and holes. The decrease in activity above 0.50 wt. % of Pd loading hence suggests that the 1-butene isomerization was depressed by the recombination. The optimum distribution of Pd atoms on the TiO_2 surface was calculated to be 0.5−1 atoms/20 nm^2 on the basis of the optimal amount of Pd (0.25−0.50 wt. %) and specific surface area of TiO_2 (300 m^2 g^{-1}).

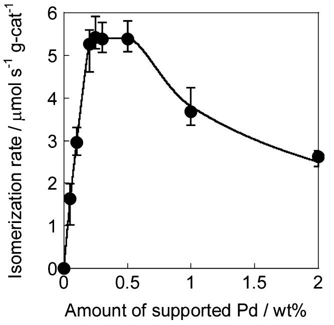

Figure 6. Effects of the amounts of loaded palladium on the double-bond shift rate of 1-butene to 2-butene.

3.7. Effect of Reaction Time on cis/trans Ratio of 2-Butenes. The time course of the cis/trans ratio of 2-butenes over 0.50 wt. % Pd/TiO_2 was studied at room temperature under irradiation of UV light in the double-bond-shift isomerization of 1-butene. The results are shown in Figure 7. The cis/trans ratio gradually decreased from 1.8 to 0.3 with an

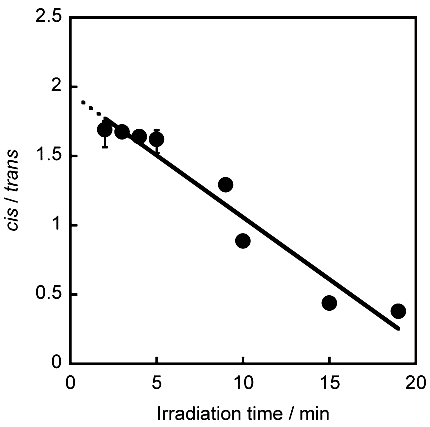

Figure 7. Time courses of the ratio of *cis*-2-butene to *trans*-2-butene over 0.50 wt. % Pd/TiO_2.

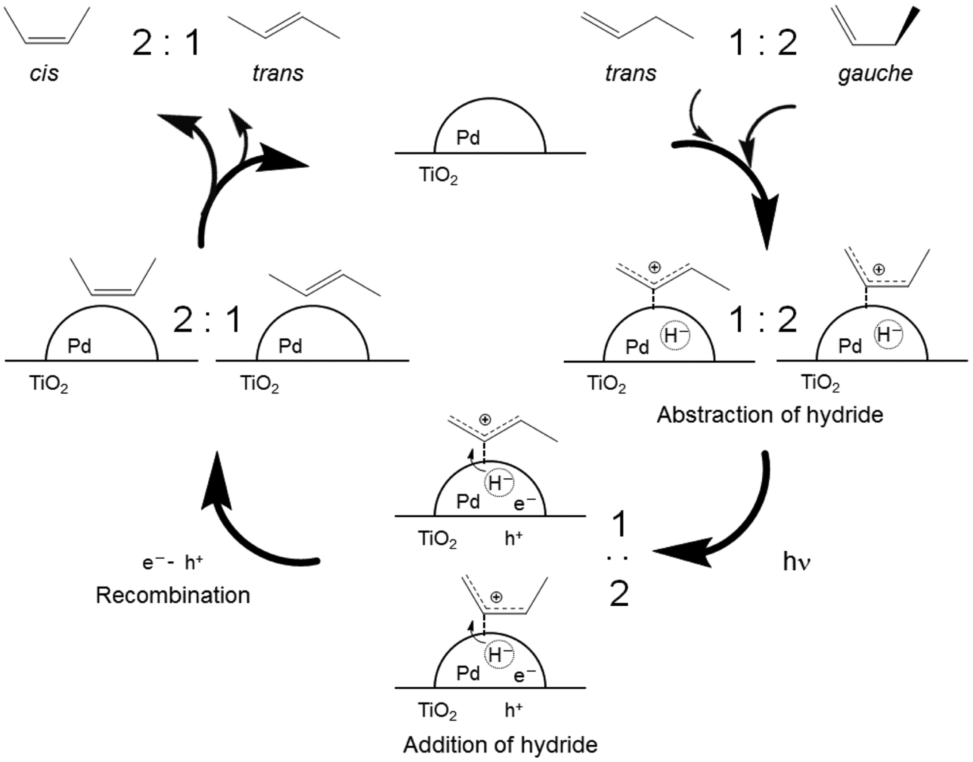

Figure 8. Proposed isomerization scheme of 1-butene (formation of 2-butenes) over Pd/TiO_2.

increase in reaction time. Since the ratio is 0.3 at 298 K at a thermal equilibrium, the ratio, 1.8, is an abnormal value. If the ratio extrapolates to an initial time of zero, the value is estimated to become closer to 2.

3.8. Function of Pd/TiO_2 under UV irradiation. Double-bond isomerization is a typical acid−base catalytic reaction. The relations between catalytic acid−base properties and product distribution in the double-bond-shift isomerization of 1-butene to its isomers were studied in detail.[22−34] The isomerization is often used as a standard test reaction for characterizing acid−base catalysts. Butenylcarbenium ion is formed by abstraction of hydride ion as a first intermediate of 1-butene isomerization over Lewis acid-catalysts. Although the C═C double bond does not undergo strong sp^3 rehybridization because of the formation of a di-σ bonded complex typically seen for alkenes on a metal surface, the double-bond features of the C_2−C_3 bond in the carbenium ion are much stronger than those of the C_2−C_3 bond in methyl π-aryl anion that is formed over Lewis basic-sites by abstraction of proton as an intermediate. Therefore, geometrical isomerization between *cis*-type and *trans*-type carbenium ions hardly occurs in the butenylcarbenium ion; methyl π-allyl anion prefers *cis*-2-butene to *trans*-2-butene in contrast to features of the butenylcarbenium ion. Furthermore, the gauche form of 1-butene adsorbs on the catalyst to generate *cis*-type butenylcarbenium ion, whereas the *trans* form of 1-butene adsorbs to generate *trans*-type butenylcarbenium ion, that is, the geometrical structure of the adsorbed butenylcarbenium ion strongly depends on the pristine structure of starting 1-butene. Therefore, gauche and *trans* forms of 1-butene transform to *cis*- and *trans*-2-butenes, respectively, in the double-bond-shift isomerization over Lewis acid. Since the ratio of gauche form to *trans* form is 2 at equilibrium in gaseous 1-butene, the ratio of *cis*- to *trans*-2-butene becomes 2 in an incipient isomerization, while for Bränsted acid and Lewis base catalysts, the ratios of the isomers have been reported to be 1 and above 3, respectively.[35,36] The obtained value agrees with the value for the ratio of gauche form to *trans* form in starting 1-butene, strongly suggesting that the photocatalytic isomerization mechanism of 1-butene over Pd/TiO_2 is similar to that over Lewis acid.

It is known that butenylcarbenium ion is formed by abstraction of hydride from 1-butene as the intermediate on the surface of a Pd metal and that both the carbenium ion and dissociated hydrogen adsorb competitively at room temperature in the presence of hydrogen.[37−45] In fact, the generation of butenylcarbenium ion was confirmed by of the IR data shown in Figure 2. Furthermore, the ratio of gauche form to *trans* form is reflected in the double-bond-shift isomerization over Pd/TiO_2. We previously reported that photogenerated electrons in the conduction band of TiO_2 transferred to Pd particles in photocatalytic dehydrogenation of benzyl alcohol to benzaldehyde over Pd/TiO_2.[46] In addition, the isomerization might depend on the Fermi level in Pd particles, because the increase in recombination accompanies a decrease in the Fermi level. Considering these results and results presented in the literature, the working mechanism of the double-bond-shift isomerization of 1-butene over Pd/TiO_2 under UV irradiation can be proposed as illustrated in Figure 8: (1) 1-Butene adsorbs on Pd/TiO_2 and butenylcarbenium ion is formed by abstraction of hydride, (2) photogenerated electrons transform to Pd particles under irradiation of UV light followed by addition of hydride to the butenylcarbenium ion, (3) 2-butenes are formed and then electrons and holes recombine, and (4) 2-butenes are eliminated to the gas phase. In the double-bond-shift isomerization of 1-butene over Pd/TiO_2, it is obvious that addition of hydride to the butenylcarbenium ion in process 2 is a key reaction. A high Fermi level in the Pd particles would be required for the addition of hydride to butenylcarbenium ion adsorbed on Pd particles. Since this reaction did not occur in the dark even at 373 K, photogenerated electrons would strongly contribute to the increase in Fermi level in Pd particles, resulting in addition of hydride to the butenylcarbenium ion. In the proposed working mechanism, photogenerated electrons and holes finally recombine after addition of hydride to the butenylcarbenium ion, resulting in the formation of 2-butenes. As mentioned in section 3.4 and shown in Figure 3, an extremely high value of AQE (72% at 348 nm) was observed. The value is acceptable if the reaction proceeds through the proposed working mechanism. Since the Fermi level in Pd particles is dependent on the recombination, the effect of the amount of Pd on the rate of isomerization shown in Figure 6 would be related to the Fermi level. The Fermi level was increased by only a small amount of Pd loading (0.25−0.50 wt. %), which resulted in a larger rate of isomerization, assuming that the addition of hydride to the butenylcarbenium ion is a rate-controlling step. The decrease in Fermi level because of the increase in recombination by excess loading of Pd hence depresses the addition rate. There are some factors other than Fermi level controlling this reaction and these factors would affect one another. Therefore, we think that charge separation ability, ability for abstraction of hydride from 1-butene, Fermi level and other properties of Pd metal are most highly balanced among the metals examined in this study. In other words, metals other than Pd should exhibit certain levels of activity even though these properties are not well balanced. In fact, as shown in Table 1, 1-butene slightly converted over Cu, Rh, and Pt, and the yields were dependent on the kind of metals. Another working mechanism of the double-bond-shift isomerization of 1-butene over Pd/TiO_2 under UV irradiation can be also considered: (1) the abstracted hydride reacts with positive holes, resulting in formation of hydrogen atoms at the interface between Pd particles and the TiO_2 surface and (2) thus-formed hydrogen atoms are reduced by photogenerated electrons to give hydride. However, this mechanism is less plausible because contribution of holes is indispensable to achieve isomerization. Taking into account the extremely large value of AQE in this reaction and the large difference in the mobility of photogenerated electrons and holes, the former mechanism shown in Figure 8 is more plausible.

■ CONCLUSIONS

Rapid isomerization of 1-butene to *cis*-2-butene and *trans*-2-butene occurred over Pd/TiO_2 under irradiation of UV light: the isomerization was drastically accelerated by a slight loading of Pd, and the rate over 0.50 wt. % Pd/TiO_2 was 8000-times larger than that over bare TiO_2. The ratio of *cis*-2-butene to *trans*-2-butene was about 2 at initial isomerization and the ratio was equal to the ratio obtained by Lewis acid catalysts. The photoisomerization over Pd/TiO_2 could be controlled by the intensity of UV light. It is effective for acid−base reaction to use a Pd/TiO_2 photocatalyst as a controllable substitute for a Lewis acid catalyst with light.

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Notes

The authors declare no competing financial interest.

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