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Anti-Markovnikov hydration of alkenes over platinum-loaded titanium oxide photocatalyst⁺

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Hydration of various alkenes proceeded over a platinum-loaded titanium oxide photocatalyst. It is notable that, unlike conventional acid-catalysts, the photocatalyst preferentially promoted the hydration according to the anti-Markovnikov rule. The results of some reaction experiments and semiempirical molecular orbital calculations suggested the reaction path of this hydration as follows: an electrophilic surface oxygen radical species formed on the photoexcited titanium oxide attacks a carbon double bond of the alkene to produce an intermediate, followed by the addition of a hydrogen radical formed on the platinum sites to produce an alcohol. The anti-Markovnikov selectivity for each investigated alkene would be determined by the stability of the radical intermediate.

1. Introduction

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Hydration of alkenes (water addition to carbon double bond) is an important industrial process for the direct synthesis of alcohols, which are widely used as the chemical intermediates for resins, agricultural chemicals, surfactants, and so on. Although the selective hydration to produce branched alcohols is possible by using homogeneous and heterogeneous acid catalysts, e.g., sulfonic acid,^{1a} heteropolyacid,^{1b} zeolite,^{1c} ionexchanged resin,^{1d} etc., the acid catalysts are unable to produce primary alcohols (except for ethylene to ethanol) or less substituted alcohols because of the strict regioselectivity known as the Markovnikov rule. According to this rule, as shown in eqn (1),² the proton (H^+) is firstly added to the carbon bonding to less alkyl substituents in the carbon double bond, followed by the addition of a functional group (X⁻, anion or neutral molecule) to the carbon with more alkyl substituents. In the case of the hydration, after the addition of the proton, a water molecule adds to the carbocation intermediate, followed by the deprotonation. This selectivity is determined by the stability of the carbocation intermediate.

On the other hand, various processes to produce anti-Markovnikov type alcohols from alkenes have been studied

$$\begin{array}{c} R_{1} \\ R_{2} \\ R_{2} \end{array} \xrightarrow{H^{+}} \begin{array}{c} R_{1} \\ R_{2} \end{array} \xrightarrow{R_{1}} \begin{array}{c} X^{-} \\ R_{2} \end{array} \xrightarrow{R_{1}} \begin{array}{c} X^{-} \\ R_{2} \end{array} \xrightarrow{R_{2}} \begin{array}{c} R_{1} \\ R_{2} \end{array} \xrightarrow{R_{2}} (1)$$

for a long time. Hydroboration by borane reagents followed by oxidation,³ and hydroformylation by transition metal catalysts⁴ followed by hydrogenation are the very famous routes to give the excellent anti-Markovnikov selectivity. However, both are multistep processes and especially the former consumes the boranes. Recently, one-pot syntheses of primary alcohols have been attained, e.g., successive hydroformylation/hydrogenation with the Rh/xantphos and Shvo's catalyst,⁵ and Wacker-type oxidation/hydrolysis/hydrogenation with the PdCl₂ and Shvo's catalyst.⁶ In these syntheses, however, strictly defined reaction conditions were required for each elementary process. So far, direct hydration processes have been realised only for the alkenes having an electron withdrawing group, such as photohydration of nitro-substituted styrenes in the presence/absence of a photosensitiser,^{7a} photohydration of 1,1-diphenylpropene in the presence of a photosensitising cyclodextrin host,^{7b} and hydration of such alkenes with phosphine catalysts.⁸ Thus, the development of new simple processes that follow the anti-Markovnikov rule are still required.

Photocatalysis has received much attention because of its unique potential to enable various organic syntheses in mild conditions by using photoformed hole (h^+) and electron (e^-),⁹ and could directly produce alcohols from alkanes (cyclohexane, *etc.*) on titanium oxide,^{10a} V₂O₅/Al₂O₃,^{10b} Cr–Si binary oxide,^{10c}

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CuCl₂,^{10d} and so on. However, primary alcohols were obtained as minor products.^{10b,d} To our knowledge, photocatalytic hydration of alkenes has not been reported yet.

In our previous study, we succeeded in the selective aromatic ring hydroxylation by using water with a platinum-loaded titanium oxide photocatalyst and clarified that the oxygen radical species produced from water were electrophilic.¹¹ Thus, in the present study, we applied this photocatalytic system to the hydration of alkenes, and found that the photocatalytic hydration of alkenes proceeded and the regioselectivity preferentially followed the anti-Markovnikov rule.

2. Experimental section

2.1. Reagents

Titanium oxide sample, JRC-TIO-8 (anatase, 338 m² g⁻¹) and JRC-TIO-6 (rutile, 100 m² g⁻¹) were supplied by Catalysis Society of Japan and the former was used unless stated. Precursors of the cocatalyst were chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O, Kishida, 99.9%), palladium chloride (PdCl₂, Kishida, 99%), and gold chloride acid tetrahydrate (HAuCl₄·4H₂O, Kishida, 99%). These reagents were used without further purification. Other reagents were 1-butene (TCI, 98%), 1,3-butadiene (TCI, 95%), 1-hexene (Aldrich, 99%), cyclohexene (Wako, 97%), 1-methyl-1-cyclohexene (TCI, 98%), 2-methyl-1,3-butadiene (TCI, 99%), 1,5-hexadiene (TCI, 97%), thiophene (Aldrich, 99%), D₂O (Acros Organics, 99.95%), and H₂¹⁸O (Euriso-top, 95.4%). These reagents were used after purification by distillation, except for the isotopic-labeled water.

2.2. Preparation of metal-loaded titanium oxide photocatalysts

Metal-loaded titanium oxide was prepared by a photodeposition method. The titanium oxide powder (4 g) was dispersed into an aqueous methanol solution (400 ml, methanol concentration 25%) containing the metal precursor in a 500 ml beaker with vigorous stirring, followed by irradiation from the top with a 300 W xenon lamp, which emitted both UV and visible light, at room temperature for 3 h. Then, the suspension was filtered off with suction, washed with water, and dried at 323 K overnight. In this article, *x* wt% of metal (M)-loaded titanium oxide is described as $M(x)/TiO_2$. Measurements of ICP-AES with an Optima 3300 DV (Perkin-Elmer Japan) confirmed that the objective amount of metal was correctly loaded on the titanium oxide. The average platinum particle size on the Pt/TiO₂ samples was estimated by using a CO-pulse method in a flow system after the reductive pretreatment with hydrogen at 423 K for 20 min.

2.3. Photocatalytic reaction tests

Photocatalytic reaction tests were carried out by using two kinds of reactors; one was a closed reactor connected with a vacuum line and the other was a closed reactor connected with an argon gas flow line. In the former system, the photocatalytic reactions of gaseous substrates were investigated. The prepared $M(x)/TiO_2$ sample in a quartz cell was irradiated with the 300 W xenon lamp from beneath in an air atmosphere for 1 h followed

by evacuation. Then, a gaseous substrate (1-butene or 1,3butadiene, 1.8 mmol) and liquid water (mainly 10 ml, corresponding to 560 mmol) were introduced to the cell, where the substrate should be partly dissolved in the water and the photocatalyst also existed in the liquid phase, and the cell was irradiated with the 300 W xenon lamp with magnetic stirring of the liquid phase at 314 K. After the irradiation, the gas phase products were collected by a gas tight syringe and analysed by a GC-TCD (Shimadzu, GC-8A). Then, the products in the liquid phase were analysed by a GC-MS (Shimadzu, QP-5050A) and a GC-FID (Shimadzu, GC-14B). In the latter reactor, liquid substrates were investigated. The prepared $Pt(0.1)/TiO_2$ sample in the quartz cell was irradiated with the 300 W xenon lamp for 1 h in the presence of air. After the air in the reactor was purged by argon, the substrate (1.0 ml, corresponding to 8.0-10 mmol) except for thiophene (2.0 ml, corresponding to 24 mmol) and water (1.0 ml or 10 ml) were introduced to the cell, and the cell was irradiated with the 300 W xenon lamp in an argon atmosphere with magnetic stirring at 314 K for 60 or 180 min. After the irradiation, the gas phase products were analysed by the GC-TCD (Shimadzu, GC-8A). Then, methanol was added to the liquid phase and analysed by the GC-MS (Shimadzu, QP-5050A) and the GC-FID (Shimadzu, GC-14B). In both systems, when the irradiation light wavelength was limited, an optical band pass filter permitting the light transmission of 360 ± 5 nm in wavelength or a cut-off filter permitting that of longer than 370 nm in wavelength was used and the reaction temperature was 305 K. As the control experiments, reaction tests without the photocatalyst or the photoirradiation were also carried out in the absence of the photocatalyst or in the dark. These experiments confirmed that the detected products in this article were produced by the photocatalysis on the $M(x)/TiO_2$ samples.

3. Results and discussion

3.1. Outline of the photocatalytic reaction

Table 1 shows the result of the photocatalytic reaction of 1,3butadiene over the $M(0.1)/TiO_2$ samples. We found that some kinds of metal-loaded TiO2 photocatalysts were able to promote hydration of 1,3-butadiene. When the $Pt(0.1)/TiO_2$ sample was used under irradiation without the limitation of the wavelength (Table 1, entry 1), the products were 5.6 μ mol of primary alcohols (2-butne-1-ol and 3-butene-1-ol), and 1.4 µmol of 2-butenal, 3.2 µmol of coupling products and an excess amount (110 µmol) of hydrogen, and thus the alcohol selectivity was low (42%). On the other hand, when the irradiation wavelength was limited to 360 ± 5 nm, the coupling products and the excess amount of hydrogen was suppressed and the higher alcohol selectivity (76%) was obtained (Table 1, entry 2). This would be mainly because the direct photoexcitation of 1,3-butadiene adsorbed on the titanium oxide resulting in the formation of byproducts was suppressed.^{11b} It is notable that, although the hydration reaction with various acid catalysts usually follows the Markovnikov rule,¹ the current photocatalytic hydration of 1,3-butadiene proceeded according to the anti-Markovnikov

Table 1 Results of the reaction tests for the photocatalytic hydration of 1,3-butadiene over the M(0.1)/TiO₂ samples



^{*a*} Coupling products, mainly C₈ hydrocarbons. The yields of other coupling products were very small. ^{*b*} Alcohol yield (%) = 100 × $Y_{Alcohols}$ /(introduced 1,3-butadiene), where Y stands for the yielded amount of product. ^{*c*} Alcohol selectivity (%) = 100 × ($Y_{Primary alcohols} + Y_{2-Butanol}$)/($Y_{Primary alcohols} + Y_{2-Butanol} + Y_{Alehydes} + Y_{2-Butanol} + 2 × <math>Y_{Coupling products}$). ^{*d*} Anti-Markovnikov selectivity (%) = 100 × ($Y_{Primary alcohols} + Y_{2-Butanol}$)/($Y_{Primary alcohols} + Y_{2-Butanol} + Y_{Alehydes} + Y_{2-Butanol}$). ^{*e*} Catalyst, 0.2 g; 1,3-butadiene, 1.8 mmol; water, 10 ml (560 mmol); reaction time, 180 min; reaction temperature, 314 K; irradiated light wavelength was not limited. Irradiated light intensities were 13, 54, and 148 mW cm⁻² when measured at 254 ± 10, 365 ± 15, and 405 ± 30 nm, respectively. The detection limits of the organic compounds, hydrogen and carbon dioxide were 0.01, 0.1 and 1.0 µmol, respectively. ^{*f*} The left and right values in the parenthesis correspond to the yield of 3-buten-1-ol and 2-butene-1-ol, respectively. ^{*g*} The left and right values in the parenthesis correspond to the yield of 3-buten-1-ol and 2-butene-1-ol, * Reaction temperature, 305 K; irradiated light wavelength, 360 ± 5 nm; irradiated light intensity was 8.4 mW cm⁻² when measured at 365 ± 15 nm. The other conditions were the same as the footnote e.

rule very selectively (almost 100%) regardless of the irradiated light wavelength (Table 1, entries 1 and 2), *i.e.*, only primary alcohols were produced while no secondary alcohols were observed. In addition, such high anti-Markovnikov selectivity was also observed on the samples with the other loading metals, such as palladium and gold (97 and 100%, Table 1, entries 3 and 4), although they promoted the reaction with less alcohol selectivity even under the light of limited wavelength.

Table 2 shows the results of the photocatalytic reaction tests of various alkenes in the optimised conditions for each substrate. From all of the investigated alkenes, the corresponding alcohols were produced, indicating that this photocatalytic system is available for various alkenes in both gas and liquid states. The alcohols were observed in the liquid phase in each case. Further, the anti-Markovnikov type products were preferentially (65-100%) produced from all of the substrates except for the cyclohexene having a symmetric double bond, although the anti-Markovnikov selectivity was different between the listed substrates. This will be discussed later. In the case of 1-methyl-1-cyclohexene, the alcohol according to the anti-Markovnikov rule (1.2 µmol) consisted of cis- and trans-isomers of similar amounts, 0.7 and 0.5 µmol, respectively (Table 2, entry 5), which will be also discussed later. For the cyclohexene, the alcohol selectivity was especially low (17%) because it is difficult to inhibit the coupling reaction in this condition. For the other substrates, the alcohol selectivity widely varied (38-83%) because of the yield of the carbonyl compounds.

Fig. 1 shows the effect of the platinum loading amount on the photocatalytic reaction of 1,3-butadiene. As shown in Fig. 1a, the highest amount of alcohol was obtained on the $Pt(0.1)/TiO_2$ sample. In principle, the smaller platinum nanoparticles

having a larger work function would be effective for the separation of the photoformed hole–electron pairs, and the larger amount of such effective small nanoparticles would provide the best performance.¹² The size and number of the platinum nanoparticles determined by the CO adsorption method were shown in Fig. 1c. The $Pt(0.1)/TiO_2$ sample had the largest number of platinum nanoparticles with the almost smallest size among them, which agrees with the above discussion. On the other hand, the high anti-Markovnikov selectivity did not vary with increasing platinum loading amount although the average diameter of the platinum also increased (Fig. 1b and c). Thus, the loading amount, *i.e.*, the diameter and the number of the platinum nanoparticles, would not be the controlling factor for the anti-Markovnikov selectivity, as discussed later.

Fig. S1 and S2, (ESI[†]) show the influence of the crystal phase and the specific surface area of titanium oxide on the photocatalytic activity for the hydration of 1-hexene (Fig. S1, ESI⁺) and thiophene (Fig. S2, ESI[†]). As for the specific surface area of the $Pt(0.1)/TiO_2(anatase)$ sample, the total yield increased with increasing the specific surface area while the anti-Markovnikov selectivity was almost constant for both substrates (Fig. S1b and S2b, ESI[†]). This would be because catalytically active sites on the titanium oxide would increase with increasing the specific surface area as reported in the literature.^{12,13} As for the crystal phase of titanium oxide, the anatase exhibited higher photocatalytic activity than the rutile having almost the same specific surface area (Fig. S1b and S2b, ESI[†]). Since the potential of the photoformed hole in the rutile $(3.04 \text{ V} \text{ vs. NHE})^{14a}$ is lower than that in the anatase (3.12 V vs. NHE),^{14b} the rutile would less promote the oxidation of water (e.g., $H_2O + h^+ \rightarrow {}^{\bullet}OH + H^+$, 2.8 V vs. NHE)^{14c} than the anatase. Thus, anatase titanium

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Table 2Results of the reaction tests for the photocatalytic hydration of various alkenes over the $Pt(0.1)/TiO_2$ sample

^{*a*} Catalyst, 0.2 g; substrate, 1.0 ml (8.0–9.9 mmol); water, 1.0 ml (56 mmol); reaction time, 60 min; reaction temperature, 305 K; irradiated light wavelength, > 370 nm; irradiated light intensities were 3, 10 and 84 mW cm⁻² when measured at 254 ± 10 , 365 ± 15 and 405 ± 30 nm, respectively. The detection limit of the organic compounds was 0.01 µmol, that of hydrogen was 0.1 µmol, and that of carbon dioxide was 1.0 µmol. ^{*b*} CP = coupling products. ^{*c*} Alcohol yield (%) = $100 \times Y_{Alcohols}/(introduced substrate)$, where *Y* stands for the yielded amount of product. ^{*d*} Alcohol selectivity (%) = $100 \times Y_{Alcohols} + Y_{Carbonyl products} + 2 \times Y_{CP}$). ^{*e*} Anti-Markovnikov selectivity (%) = $100 \times (Y_{Anti-Markovnikov type alcohol + Y_{Anti-Markovnikov type carbonyl product})/(Y_{Alcohols} + Y_{Carbonyl products}). ^{$ *f*} Dimer (*C*₁₂) hydrocarbons were produced. The detailed structure was not analysed. ^{*g* $} Catalyst, 0.2 g; substrate, 1.0 ml (8.4–10 mmol); water, 10 ml (560 mmol); reaction time, 180 min; reaction temperature, 305 K; irradiated light wavelength, <math>360 \pm 5$ nm; irradiated light intensity was 8.4 mW cm⁻² when measured at 365 ± 15 nm. ^{*h*} Also detected was 10 µmol of carbon dioxide. ^{*i*} The left and right values in the parenthesis corresponds to the yield of unsaturated and saturated alcohol in the two structural formulas. ^{*j*} 1-Butene, 1.8 mmol; water, 10 ml (560 mmol); the other conditions were the same as the footnote g. ^{*k*} n.d. = not detected. ^{*l*} 5-Methyl undecane. ^{*n*} Thiophene, 2.0 ml (24 mmol); water, 8.0 ml (440 mmol); reaction time, 60 min; reaction temperature, 314 K; irradiated light intensities were 23, 80, and 176 mW cm⁻² when measured at 254 ± 10 , 365 ± 15 and 405 ± 30 nm, respectively. Also detected was 18 µmol of carbon dioxide. ^{*o*} Bithiophenes. ^{*p*} Dimer (*C*₁₀) hydrocarbons were produced. The detailed structure was not analysed.

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Fig. 1 The effect of the platinum loading amount on the products yield (a) and selectivity (b) in the photocatalytic hydration of 1,3-butadiene over the $Pt(x)/TiO_2$ samples. The red filled circles, red blank triangles, green filled squares and black filled diamonds in panel a correspond to the total yield of 2-butene-1-ol and 3-butene-1-ol, that of 2-butenal and butanal, that of the coupling products, and the yield of hydrogen, respectively. The orange filled inverse triangles and orange blank inverse triangles in panel b correspond to the anti-Markovnikov selectivity and the alcohol selectivity, respectively. The blue blank circles and pink blank squares in panel c correspond to the average diameter and the number of the platinum nanoparticles, respectively. The average diameter of the platinum nanoparticles was determined by the CO pulse method. As for the reaction conditions, see the footnote a of Table 1.

oxide with a large surface area would be most effective for the hydration.

The magnitude of the influence by the specific surface area was different between the substrates, which would be derived from the properties of the substrates although the details were not clarified in the present study.

3.2. Active species

Table 3 shows the results of the isotopic experiments in the photocatalytic hydration of cyclohexene. When the reaction was carried out by using D_2O , the mass number (*m*/*z*) of the molecular ion peak for most of the produced cyclohexanol (>99%) increased from 100 to 101 (Table 3, entry 1). In the present analysis method, the D atom of the hydroxyl group in the produced alcohol can be easily exchanged with the H atom of methanol that was added for homogenisation of the liquid phase after the reaction before the analysis. Thus, the increase of the mass number would originate from the D atom of D_2O , which was directly added to the carbon double bond. This result suggests that the alcohol was dominantly produced through photocatalytic hydration (water addition) of the carbon double bond as shown in eqn (2).

$$R$$
 + H₂O $\frac{h\nu}{Pt/TiO_2}$ HO R or R (2)

Table 3 Results of the isotopic experiments in the photocatalytic hydration of cyclohexene over the $Pt(0.1)/TiO_2$ sample^a



^{*a*} Catalyst, 0.2 g; cyclohexene, 1.0 ml (9.9 mmol); water, 1.0 ml (56 mmol); reaction time, 60 min; reaction temperature, 305 K; irradiated light wavelength, >370 nm; irradiated light intensities were 3, 10 and 84 mW cm⁻² when measured at 254 ± 10, 365 ± 15 and 405 ± 30 nm, respectively. The detection limit of the organic compounds was 0.01 µmol. ^{*b*} In the present analysis method, the D atom of the hydroxyl group in the produced alcohol can be exchanged easily with H of the methanol that was introduced for analysis after the reaction. ^{*c*} n.d. = not detected. ^{*d*} Before the reaction, the photocatalyst was evacuated at 473 K for 2 h to remove the physisorbed water on the Pt(0.1)/TiO₂ sample.

When the reaction was carried out by using $H_2^{18}O$, the produced cyclohexanol contained 87% of ¹⁸O atom and 13% of ¹⁶O in the hydroxyl group (Table 3, entry 2). This indicates that the introduced water dominantly reacts with the alkene, while the lattice oxygen on the titanium oxide surface also

reacts with the alkene. In the literature,¹⁵ it was reported that upon photoirradiation the reaction between water molecules and the titanium oxide surface could produce an active surface oxygen species and the mechanism in the aqueous solution of acidic or neutral pH was proposed as follows: a bridging Ti–O–Ti site on the surface would trap the photoformed hole, and receive the nucleophilic attack of water to produce the surface oxygen radical (eqn (3)). The surface oxygen radical species would have an electrophilic property and preferably attack the carbon double bond having high electron density.^{11b}

$$T_{1} \sim O_{T_{1}} + H_{2}O + h^{+} \longrightarrow T_{1} \sim O_{T_{1}} \rightarrow H \xrightarrow{H} T_{1} \rightarrow T_{1} \rightarrow T_{1} \qquad (3)$$

On the other hand, the photoformed electron would reduce the proton in the solution to produce a hydrogen radical at the platinum sites (eqn (4)).

$$H^{+} + e^{-} \xrightarrow{} H$$
 (4)

Considering eqn (3) and (4), and the results of the isotopic experiments (Table 3), the hydration of the carbon double bond would proceed through the addition of the electrophilic surface oxygen radical and the hydrogen radical. This implies that the reaction would preferably progress on the titanium oxide surface around the deposited platinum nanoparticles.

3.3. Radical intermediates

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To discuss the order of the addition of these two radical species to the carbon double bond, we calculated the final heat of formation of the possible intermediate species, *i.e.*, the active oxygen adduct and the hydrogen radical adduct (Table 4), by using PM7 method¹⁶ in MOPAC 2012.¹⁷ In this calculation, the hydroxyl radical (•OH) was employed instead of the surface active oxygen species (eqn (3)) in order to simplify the system because they have similar thermodynamic properties to each other.^{11b} In the case of the hydroxyl radical adduct, the radical intermediate in the anti-Markovnikov hydration (Table 4, A) was more stable than that in the Markovnikov hydration (Table 4, C) for all the investigated substrates. On the other hand, in the case of the hydrogen radical adduct, the radical intermediate in the Markovnikov hydration (Table 4, D) was more stable than that in the anti-Markovnikov hydration (Table 4, B). These results clearly indicate that if the hydrogen radical attacks first to the carbon double bond before the surface oxygen radical does, the product would not follow the anti-Markovnikov rule, which was inconsistent with the fact. Thus, it is suggested that the surface oxygen radical would be first added to the carbon double bond (eqn (5)), followed by the addition of the hydrogen radical (eqn (6)). In this way, the order of the radicals addition to the carbon double bond, *i.e.*, the surface oxygen radical and then hydrogen radical, would lead to the anti-Markovnikov products. Although one may consider another possibility instead of eqn (6), that the intermediate species abstracts a hydrogen atom from water, this could not occur because

the bond energy of O–H in water (497.10 \pm 0.29 kJ mol⁻¹ at 298 K) is larger than that of C–H in hydrocarbons (*e.g.*, butane 421.3 and 411.1 \pm 2.2 kJ mol⁻¹, cyclohexane 416.3 kJ mol⁻¹ at 298 K).¹⁸



The differences of the final heat of formation for the two possible isomers of the hydroxyl radical adduct were also listed (Table 4, A–C). It is notable that the value decreased with increasing anti-Markovnikov selectivity, meaning that a larger difference between the two possible radical intermediates resulted in a higher anti-Markovnikov selectivity. Thus, the difference of the stability between the intermediates (eqn (5)) would determine the regioselectivity of the hydroxyl group for each substrate.

3.4. Successive reactions

Table 5 shows the results of the photocatalytic reaction tests for the successive reactions of 1-butene conversion by using the alcohols and the carbonyl compounds as the reactants. Butanal and 2-butanone were converted not to alcohols but to hydrogen and carbon dioxide (Table 5, entries 1 and 2), where only the complete oxidation with water occurred. On the other hand, 1-butanol and 2-butanol were oxidised into the carbonyl compounds (Table 5, entries 3 and 4), that is, the successive oxidation could occur after the hydration. Thus, the alcohol can be oxidised to carbonyl compounds as shown in eqn (7), and further oxidised to the final products, *i.e.*, hydrogen and carbon dioxide.

HO,
$$R$$
 or R $h\nu$ Pt/TiO_2 R or R + H₂ (7)

Fig. 2 shows the time course of the products yield in the photocatalytic hydration of 1-butene in the closed reactor. Although the total production rate of the alcohols and the carbonyl products decreased once after 1 h, it became constant at least until 24 h (Fig. 2b, purple filled squares). It is notable that the carbonyl compounds were produced at a constant rate even in the initial stage of the photocatalytic reaction. If the carbonyl compounds were produced only through the successive oxidation of the alcohols (eqn (7)), the production of the carbonyl compounds should be delayed compared to that of the alcohols, which is inconsistent with the results. Thus, the carbonyl compounds are also produced directly and competitively. In the previous study for the aromatic ring hydroxylation,^{11b}

Table 4 Relationship between anti-Markovnikov selectivity in the photocatalytic hydration and the final heat of formation of the possible radical intermediates^a

		Final heat of formation/kJ mol ⁻¹						
		Anti-Markovnikov type		Markovnikov type		Difference		Anti Markarnikar
Entry	Substrate	•OH adduct (A)	•H adduct (B)	•OH adduct (C)	•H adduct (D)	(A–C)	(B-D)	selec. ^{<i>b</i>} (%)
1		но	H	OH	н,	-12.4	27.4	65
		-89.5	99.0	-77.1	71.6			
2		HO	H	OH	H,	-19.6	26.8	72
		-163.0	25.1	-143.4	-1.74			
3	$\sim\sim$	HO	H	OH	H	-20.1	27.2	75
		-205.9	-17.2	-185.8	-44.4			
4		HO	H X	HO	H —	-21.1	12.2	81
		-218.8	-19.9	-197.7	-42.1			
5	$\langle \mathbf{s} \rangle$	С, S ОН	K.	CH S	ς. Υ	-24.0	21.7	100
		-38.4	151.9	-14.4	130.2			
6		HO	H	OH	H	-46.8	56.4	100
		-74.5	142.4	-27.7	86.0			
7 ^c	.	HO	H	OH	H	-50.7	51.3	100
		-111.2	102.3	-60.5	51.0			
8		HO	·H	· OH	H	-57.1	76.8	100
		-113.5	121.8	-56.4	45.0			

^{*a*} Final heat of formation was calculated by PM7 method¹⁶ in MOPAC2012.¹⁷ As for the reaction conditions, see the footnotes in Tables 1 and 2. ^{*b*} See the foot note e in Table 2.

it was suggested that the hydrogen atom could be abstracted from the intermediate by a radical species. In a similar way, the carbonyl compounds would be produced through the abstraction of hydrogen from the intermediate species as shown in eqn (8).



Considering these reaction routes to produce carbonyl compounds (eqn (7) and (8)), the regioselectivity of the carbonyl group would be the same as that of the hydroxyl group in the produced alcohol because of the difference of the stability between the intermediates as mentioned above.

3.5. Effect of water quantity

Fig. 3 shows the influence of water quantity on the photocatalytic hydration of 1-butene as a gaseous reactant, where it was a three phase reaction system (gas–liquid–solid). With increasing the quantity of the liquid water to 10 ml in volume,

 Table 5
 Results of photocatalytic reaction tests of hydration products over the Pt(0.1)/TiO2 sample^a

		Products/µmol							
Entry	Substrate	HO	H H	OH	o	H_2	CO_2		
1	H H	n.d.	4.8	n.d.	n.d.	54	11		
2	°,	n.d.	n.d.	n.d.	6.8	43	8.2		
3	HO	13.0	7.6	n.d.	n.d.	54	4.9		
4	ОН	n.d.	n.d.	14.2	4.7	51	5.6		

^{*a*} Catalyst, 0.2 g; substrate, 25 μmol in the aqueous solution (10 ml); reaction time, 180 min; reaction temperature, 314 K; light intensities were 13, 54, and 148 mW cm⁻² when measured at 254 \pm 10, 365 \pm 15, and 405 \pm 30 nm, respectively. n.d. = not detected.



Fig. 2 The time course of the products yield (a), and the total yield and selectivity (b) in the photocatalytic hydration of 1-butene over the $Pt(0.1)/TiO_2$ sample. The red filled circles, red filled triangles, blue blank circles, blue blank triangles, black filled diamonds and pink blank diamonds in panel a correspond to the yields of 1-butanol, butanal, 2-butanol, 2-butanone, hydrogen and carbon dioxide, respectively. The purple filled squares, orange filled inverse triangles and orange blank inverse triangles in panel b correspond to the total yield of the alcohols and the carbonyl products, the anti-Markovnikov selectivity and the alcohol selectivity, respectively. Catalyst, 0.2 g; 1-butene, 1.8 mmol; water, 10 ml (560 mmol); reaction temperature, 314 K; irradiated light intensities were 13, 54, and 148 mW cm⁻² when measured at 254 \pm 10, 365 \pm 15 and 405 \pm 30 nm, respectively.

the yield of the alcohols and carbonyl products increased and that of excess hydrogen decreased (Fig. 3a). In addition, the alcohol selectivity and the anti-Markovnikov selectivity also increased. When the introduced amount of water was very



Volume of water / ml

Fig. 3 The influence of water quantity on the photocatalytic hydration of 1-butene over the Pt(0.1)/TiO₂ sample. The red filled circles, red filled triangles, blue blank circles, blue blank triangles and black filled diamonds in panel a correspond to the yields of 1-butanol, butanal, 2-butanol, 2-butanone and hydrogen, respectively. The orange filled inverse triangles and orange blank inverse triangles in panel b correspond to the anti-Markovnikov selectivity and the alcohol selectivity, respectively. Catalyst, 0.2 g; 1-butene, 1.8 mmol; reaction time, 180 min; reaction temperature, 314 K; light intensities were 13, 54, and 148 mW cm⁻² when measured at 254 \pm 10, 365 \pm 15 and 405 \pm 30 nm, respectively.

small (1.0 ml), the color of the catalyst changed, implying that undetectable byproducts (*e.g.*, coupling products) would be produced from the 1-butene and the hydration products. This means that the presence of water would contribute to not only the formation of alcohol and carbonyl products (eqn (9) and (10)) but also the desorption of the products from the surface as a solvent to prohibit the excess adsorption of the products and side reactions such as successive oxidation and coupling reactions.



On the other hand, when the volume of water was larger than 10 ml, the yield of the hydration products decreased although the selectivity was not changed. With an increased volume of water in the closed system, the decreased concentration of 1-butene in the aqueous solution might reduce the reaction rate.

3.6. Proposed reaction mechanism

From the above investigations and our previous study, the proposed reaction mechanism of the photocatalytic hydration of the carbon double bond is summarised in Fig. 4. In the current three phase reaction systems (gas-water-solid or oilwater-solid), the catalyst obviously exists in the aqueous phase. Thus, water molecules are always adsorbed on the titanium oxide surface (Fig. 4, i). The titanium oxide is photoexcited to produce an electron and a hole, and then the electron migrates to the platinum sites and the hole is trapped by the surface bridge oxygen sites of titanium oxide as usually proposed (Fig. 4, ii).¹⁵ The trapped hole induces the nucleophilic attack of the adsorbed water to produce a surface oxygen radical and a surface hydroxyl group. An alkene molecule would interact with the hydrogen of the adsorbed water or the surface hydroxyl group (Fig. 4, iii). The electrophilic surface oxygen radical attacks the double bond to produce a radical intermediate (Fig. 4, iv or iv'). It should be noted that the position selectivity of the surface oxygen radical to the two carbon atoms at the carbon double bond almost follows the anti-Markovnikov rule according to the stability of the radical intermediates (Fig. 4, iv). Finally, the electron in the platinum sites reduces a proton to produce a hydrogen radical, which adds to the intermediate species to produce a surface alkoxide species, and it desorbs as an alcohol (Fig. 4, v and v'), which is promoted by water. In this mechanism, the lattice oxygen atom of the titanium oxide surface is introduced to the product while the oxygen atom in



Fig. 4 The proposed reaction mechanism of the photocatalytic hydration of alkene to produce alcohol.



Fig. 5 The proposed mechanism of the photocatalytic hydration of 1-methyl-1-cyclohexene to produce the *cis*-*trans* isomers of 2-methylcyclohexanol. The above steps correspond to the steps iv and v in Fig. 4.

the water molecule is introduced to the surface in the first cycle, and then the surface oxygen atoms that originated from the water molecule are introduced into the product in the successive cycles. This is supported by the isotopic experiment with $H_2^{18}O$ (Table 3, entry 2) and the previous study.^{11b}

In this hydration reaction, anti-Markovnikov selectivity was not influenced by the platinum loading amount (the average size and the number of the platinum nanoparticle, Fig. 1). Since the key step of determining the anti-Markovnikov selectivity (the addition of the surface oxygen radical) would take place on the titanium oxide surface, this step would not be significantly influenced by the platinum loading amount.

From 1-methyl-1-cyclohexene, *cis-trans*-isomers of 2-methylcyclohexanol were produced in the present photocatalytic anti-Markovnikov hydration. The above hydration mechanism and the almost equal yields of *cis-trans* isomers suggest that the intermediate species can freely rotate in the C–O bond and be attacked by the hydrogen radical from both sides as shown in Fig. 5.

A part of the produced alcohol is further oxidised to produce carbonyl compounds probably with the formation of hydrogen (eqn (7)). On the other hand, the direct production of carbonyl compounds would competitively occur. The mechanism is proposed in Fig. S3, (ESI[†]), in which the steps (iv) and (v) are different from the above. After the formation of the intermediate (Fig. S3, iii, ESI[†]), titanium oxide is further photoexcited to form a hole and an electron (Fig. S3, iv and iv', ESI[†]). The hole abstracts the hydrogen atom from the intermediate to produce an adsorbed enoxy species (Fig. S3, v and v', ESI[†]). Finally, the enol is desorbed from the surface, and the tautomerisation occurs to produce a carbonyl compound (Fig. S3, vi and vi', ESI[†]) while the electrons in the platinum sites reduce protons to form a hydrogen molecule (Fig. S3, vii, ESI[†]).

4. Conclusion

We investigated the hydration of various alkenes (from C4 to C7, and thiophene) over the 0.1 wt% platinum-loaded titanium

oxide photocatalyst. In all of the investigated alkenes, the hydration products were obtained. Interestingly, the obtained regioselectivity of the hydroxyl group preferentially followed the anti-Markovnikov rule, *i.e.*, the primary alcohols or the less substituted alcohols were predominantly produced.

The surface oxygen participates in the present hydration to be involved in the products. For the anti-Markovnikov hydration, the order of the radical addition is important, *i.e.*, the electrophilic surface oxygen radical, which is produced through the reaction between water and the lattice oxygen of the titanium oxide surface trapping the photoformed hole, should attack the double bond of the alkene to form the radical intermediate before the addition of the hydrogen radical, which is produced from the proton and the photoformed electron on the platinum sites. At that time, the anti-Markovnikov selectivity would be determined by the stability of the radical intermediate, which depends on the nature of substrate.

The carbonyl compounds as byproducts were formed by successive oxidation or by direct photocatalytic oxidation, which also followed the anti-Markovnikov rule, since the reaction mechanism would be similar to the hydration.

The water would also function as a solvent to assist the desorption of the products, resulting in the decrease of the formation of undesired byproducts.

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Notes and References

 (a) J. L. Jensen, V. Uaprasert and C. R. Fujii, *J. Org. Chem.*, 1976, **41**, 1675; V. J. Nowlan and T. T. Tidwell, *Acc. Chem. Res.*, 1977, **10**, 252; D. J. Nelson, C. Brammer and R. Li, Tetrahedron Lett., 2009, **50**, 6454; (b) J. Poźniczek, A. M. Lubańska, A. M. Ilnicka and A. Bielański, *Appl. Catal.*, A, 1999, **176**, 101; A. V. Ivanov, E. Zausa, Y. B. Taârit and N. Essayem, *Appl. Catal.*, A, 2003, **256**, 225; G. Marcì, E. I. G. López and L. Palmisano, *Appl. Catal.*, A, 2012, **421–422**, 70; (c) D. Nuntasri, P. Wu and T. Tatsumi, *Chem. Lett.*, 2002, 224; J. Li, Z. Qin, H. Xu, M. Dong, J. Dong and J. Wang, *Ind. Eng. Chem. Res.*, 2007, **46**, 9000; X. Shan, Z. Cheng and Y. Li, *J. Chem. Eng. Data*, 2011, **56**, 4310; (d) A. Chakrabarti and M. M. Sharma, *React. Polym.*, 1992, **18**, 117; S. Talwalkar, P. Kumbhar and S. Mahajani, *Ind. Eng. Chem. Res.*, 2006, **45**, 8024; X. Shan, Z. Cheng and P. Yuan, *Chem. Eng. J.*, 2011, **175**, 423.

- 2 M. Beller, J. Seayad, A. Tillack and H. Jiao, *Angew. Chem., Int. Ed.*, 2004, **43**, 3368.
- 3 H. C. Brown and G. Zweifel, J. Am. Chem. Soc., 1961,
 83, 2544; T. C. Morrill, C. A. D'Souza, L. Yang and
 A. J. Sampognaro, J. Org. Chem., 2002, 67, 2481.
- 4 F. Ungváry, Coord. Chem. Rev., 2007, 251, 2072; F. Ungváry, Coord. Chem. Rev., 2007, 251, 2087.
- 5 K. Takahashi, M. Yamashita, T. Ichihara, K. Nakano and K. Nozaki, *Angew. Chem., Int. Ed.*, 2010, **49**, 4488.
- 6 G. Dong, P. Teo, Z. K. Wickens and R. H. Grubbs, *Science*, 2011, 333, 1609; J. Kanand, R. Paciello and M. Röper, US 6166265, 2000; L. Hintermann, *ChemCatChem*, 2012, 4, 321.
- 7 (a) P. Wan, S. Culshaw and K. Yates, J. Am. Chem. Soc., 1982,
 104, 2509; P. Wan, M. J. Davis and M. A. Teo, J. Org. Chem.,
 1989, 54, 1354; (b) G. Fukuhara, T. Mori and Y. Inoue, J. Org. Chem., 2009, 74, 6714.
- 8 I. C. Stewart, R. G. Bergman and F. D. Toste, *J. Am. Chem. Soc.*, 2003, **125**, 8696.
- 9 M. A. Fox and M. T. Dulay, *Chem. Rev.*, 1993, **93**, 341; A. Maldotti, A. Molinari and R. Amadelli, *Chem. Rev.*,

2002, **102**, 3811; O. Carp, C. L. Huisman and A. Reller, *Prog. Solid State Chem.*, 2004, **32**, 33; G. Palmisano, V. Augugliaro, M. Pagliaro and L. Palmisano, *Chem. Commun.*, 2007, 3425; Y. Shiraishi and T. Hirai, *J. Photochem. Photobiol.*, *C*, 2008, **9**, 157.

- 10 (a) P. Du, J. A. Moulijn and G. Mul, J. Catal., 2006, 238, 342;
 (b) K. Teramura, T. Tanaka, T. Hosokawa, T. Ohuchi, M. Kani and T. Funabiki, Catal. Today, 2004, 96, 205;
 (c) Y. Shiraishi, Y. Teshima and T. Hirai, Chem. Commun., 2005, 4569; (d) K. Takaki, J. Yamamoto, K. Komeyama, T. Kawabata and K. Takehira, Bull. Chem. Soc. Jpn., 2004, 77, 2251.
- (a) H. Yoshida, H. Yuzawa, M. Aoki, K. Otake, T. Hattori and H. Itoh, *Chem. Commun.*, 2008, 4634; (b) H. Yuzawa, M. Aoki, K. Otake, T. Hattori, H. Itoh and H. Yoshida, *J. Phys. Chem. C*, 2012, **116**, 25376.
- 12 H. Yuzawa, T. Mori, H. Itoh and H. Yoshida, *J. Phys. Chem. C*, 2012, **116**, 4126.
- 13 H. Kominami, S. Murakami, J. Kato, Y. Kera and B. Ohtani, *J. Phys. Chem. B*, 2002, **106**, 10501; L. Cao, Z. Gao, S. L. Suib, T. N. Obee, S. O. Hay and J. D. Freihaut, *J. Catal.*, 2000, **196**, 253.
- 14 (a) A. Shiga, A. Tsujiko, S. Yae and Y. Nakato, *Bull. Chem. Soc. Jpn.*, 1998, **71**, 2119; (b) D. Duonghong, J. Ramsden and M. Grätzel, *J. Am. Chem. Soc.*, 1982, **104**, 2977; (c) C. D. Jaeger and A. J. Bard, *J. Phys. Chem.*, 1979, **83**, 3146.
- 15 A. Imanishi, T. Okamura, N. Ohashi, R. Nakamura and Y. Nakato, J. Am. Chem. Soc., 2007, 129, 11569.
- 16 J. J. P. Stewart, J. Mol. Model., 2013, 19, 1.
- 17 J. J. P. Stewart, *MOPAC2012; Stewart Computational Chemistry*, Colorado Springs, CO, 2012, see http://openmopac.net/.
- 18 D. R. Lide, *Handbook of Chemistry and Physics*, CRC Press, London, 84th edn, 2003.

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