Transfer Channel of Photoinduced Holes on a TiO₂ Surface As Revealed by Solid-State Nuclear Magnetic Resonance and Electron Spin Resonance Spectroscopy

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1. INTRODUCTION

As the crucial step of photoreaction on TiO₂ photocatalysts, the surface transfer of photoinduced holes (h⁺) (that is, how the photoinduced holes transfer from the TiO₂ surface to adsorbed water and organic compounds on the surface active sites) has been received intensive attention in terms of photocatalytic water splitting and photocatalytic environmental cleaning. However, the ambiguous knowledge of surface active sites hinders the identification of the h⁺ transfer mechanism. Owing to the lack of direct experimental evidence, the most controversial point concerning the nature of surface active sites is whether the surface hydroxyl groups (Ti−OH) of TiO₂ can trap the photogenerated hole. Surface hydroxyl groups (Ti−OH) and adsorbed H₂O influence directly the physical and chemical properties of TiO₂ and thus may play important roles in photocatalytic reactions. It has long been assumed that the Ti−OH groups and/or adsorbed H₂O may be the surface active species, which can be oxidized by photogenerated holes (h⁺) to form a surface radical (°O−Ti and/or °OH) with high oxidation activity. In contrast, other research work speculated that it was surface lattice oxygen (bridging oxygen, Ti−O−Ti) rather than the Ti−OH groups with adsorbed H₂O that acted as the surface active species, which could trap the photogenerated h⁺ and be oxidized to form Ti−O° radicals as active paramagnetic intermediates. On the basis of experimental observations, the detailed photocatalytic mechanism of water splitting on the surface of TiO₂ was proposed.
formation of surface active sites and the \( h^+ \) transfer process has been scarcely studied by experimental methods.

It is well-known that the \( h^+ \) transfer mechanism on the TiO\(_2\) surface should involve two processes: the photoinduced holes interact with surface active sites to form active paramagnetic intermediates, and then the active paramagnetic intermediates react with surface-adsorbed molecules. As such, besides the surface active sites, the active paramagnetic intermediates also play an important role in the photoreaction. Some paramagnetic intermediates (such as \( \text{OH}^-\text{Ti}^2\text{O}^-, \text{O}_2^-\), etc.) have been experimentally observed. The \( \text{OH}^-\) radical was usually considered as the active paramagnetic intermediates which govern the photocatalytic oxidation reaction.\(^4,17,18\) Nosaka and co-workers\(^7\) pointed out that the photogenerated \( h^+ \) oxidation on the TiO\(_2\) surface produced no free \( \text{OH}^-\) radicals but adsorbed \( \text{OH}^-\) (\( \text{Ti}^+\text{OH}^-\) or \( \text{TiO}^-\)) radicals. However, it was also reported by measuring the quantum yield of \( \text{OH}^-\) radicals that their formation was not the major process on the TiO\(_2\) surface in aqueous solutions under irradiation, while the \( \text{OH}^-\) radicals were produced from the oxidation of H\(_2\)O by \( \text{O}_2^-\).\(^19\) On the other hand, some previous studies\(^20,21\) proposed that the \( \text{O}_2^-\) ion should be the active paramagnetic intermediate, which dictated the photodegradative oxidation reaction. Up to now, there have been no experimental studies on the detailed formation and transformation mechanism of various active paramagnetic intermediates in the photocatalytic H\(_2\)O splitting or H\(_2\)O oxidation, which may hinder the deep understanding of the surface photoinduced hole-transfer mechanism.

Solid-state NMR spectroscopy is a powerful tool for exploring the local environments of active sites in various photocatalysts.\(^22\)–\(^25\) Especially, the \(^1\)H MAS NMR techniques have been widely used to study the structure and distribution of hydroxyl groups and absorbed H\(_2\)O on the surface of TiO\(_2\) and other oxides.\(^26\)–\(^29\) In addition, in situ solid-state NMR has been utilized to study the photocatalytic reaction mechanism, focusing on the conversion of organic reagents on the photocatalyst surface.\(^30\)–\(^32\) However, little attention has been paid to the roles of both surface Ti–OH groups and adsorbed H\(_2\)O in the photocatalytic reaction. Hence, TiO\(_2\) photocatalysts with different Ti–OH groups and various loadings of adsorbed H\(_2\)O were studied by the solid-state NMR and electron spin resonance (ESR) techniques. One-dimensional (1D) \(^1\)H solid-state magic angle spinning (MAS) NMR was employed to identify surface hydroxyl groups and adsorbed water molecules, while two-dimensional (2D) \(^1\)H–\(^1\)H double-quantum (DQ) MAS NMR was utilized to provide the spatial proximity/interaction between them in the TiO\(_2\) photocatalysts. Combining these NMR methods with in situ \(^1\)H and \(^13\)C NMR methods, besides the reaction intermediates, the surface active center and its quantitative structure–activity relationship were identified. Furthermore, the evolution of paramagnetic intermediates on the TiO\(_2\) surface with varying H\(_2\)O loading upon irradiation was revealed for the first time by the in situ ESR technique. On the basis of the NMR and ESR results, the detailed photocatalytic mechanism of water splitting on the surface of TiO\(_2\) was proposed.

2. EXPERIMENTAL SECTION

2.1. Sample Preparation. The Pt-loaded TiO\(_2\) catalyst was prepared by in situ photodeposited reaction of H\(_2\)PtCl\(_6\) with TiO\(_2\) according to a previous report.\(^33\) Briefly, 0.2 g of TiO\(_2\) (Degussa P25, 41 m\(^2\)/g Brunauer–Emmett–Teller (BET) surface area, purchased from Sigma-Aldrich) was suspended in an aqueous solution containing H\(_2\)O (10 mL, deionized water) and H\(_2\)PtCl\(_6\)·6H\(_2\)O (0.618 mmol/L, purchased from Aladdin). After 2 h of irradiation under a 300 W Hg lamp, the gray product was collected via centrifugation, then washed by water, and dried at 333 K. The Pt/TiO\(_2\) photocatalyst (denoted as PT-1) was obtained from the gray product by dehydrating it on a vacuum system (10\(^{-3}\) Pa) at 473 K for 10 h. The PT-1 photocatalyst was further dehydrated on the vacuum system (10\(^{-3}\) Pa) at 673 K for 10 h, and the obtained sample is denoted as PT-2.

Prior to \(^1\)H MAS NMR measurements, the dehydrated photocatalysts (0.10 g) were directly transferred into 4 mm NMR rotors under a dry nitrogen atmosphere in a glovebox. To prepare the hydrated photocatalysts with different H\(_2\)O loadings, a certain amount of deionized H\(_2\)O was introduced into the dehydrated Pt/TiO\(_2\) photocatalysts (PT-1 and PT-2) in a glass tube under vacuum at the temperature of liquid N\(_2\) temperature, then the glass ampule was sealed off, and finally the sealed samples were transferred into the NMR rotors in the glovebox.

Prior to in situ NMR measurements, \(^1\)H\(_2\)OH (99% \(^13\)C, 3.0 mmol, Cambridge Isotope Laboratories, Inc.) and deionized H\(_2\)O were introduced into the dehydrated Pt/TiO\(_2\) catalyst (0.10 g) in a glass ampule under vacuum at the liquid N\(_2\) temperature. Then the glass ampule was sealed off. The photoreaction was performed in the sealed ampule under successive irradiation by a 300 W Xe lamp, and then the sealed ampule was transferred into a 7.5 mm rotor for in situ NMR measurements.

For ESR measurements, the dehydrated Pt/TiO\(_2\) photocatalysts (0.10 g) were directly transferred into a 5 mm ESR quartz tube with a vacuum valve under a dry nitrogen atmosphere in a glovebox. Different amounts of H\(_2\)O molecules were also introduced into dehydrated Pt/TiO\(_2\) photocatalysts in the ESR quartz tube under vacuum at the liquid N\(_2\) temperature. The photoreaction was performed in the quartz tube under successive irradiation by a 300 W Xe lamp for a specific reaction period (30 min). After 30 min of solar-light irradiation, 0.5 μmol of CH\(_3\)OH was introduced into the hydrated photocatalysts in the ESR quartz tube under vacuum at the liquid N\(_2\) temperature.

2.2. Characterization Methods. \(^1\)H MAS NMR experiments were carried out at 11.7 T on a Bruker-Advance\(^31\) 500 spectrometer equipped with a 4 mm double-resonance probe. The resonance frequency was 500.57 MHz. Single-pulse excitation \(^1\)H MAS experiments were performed on hydrated or dehydrated TiO\(_2\) samples, using a π/2 pulse width of 4.0 μs, a repetition time of 2 s, and a magic angle spinning rate of 10 kHz. Double-quantum coherences were excited and reconverted with the POST-C7 pulse sequence, and the excitation and reconversion time is equal to a complete C7 cycle (\( τ = 200 \mu s \)). The increment interval in the indirect dimension was set to 50 μs, and 32 t\(_1\) increments and 1024 scan accumulations for each t\(_1\) increment were used in the 2D \(^1\)H–\(^1\)H DQ MAS NMR experiments. The spin–spin relaxation time (\( T_2^* \)) of different \(^1\)H species was measured by the Hahn spin-echo technique. 2D \(^1\)H–\(^1\)H NOESY correlation NMR spectra were acquired with mixing times of 10 and 80 ms, in which the increment interval in the indirect dimension was set to 83.3 μs, and 128 t\(_1\) increments and 128 scan accumulations for each t\(_1\) increment were used.

In situ \(^1\)H and \(^13\)C solid-state MAS NMR experiments were carried out at 7.1 T on a Varian Infiniplus-300 spectrometer, equipped with a double-resonance 7.5 mm probe, with resonance frequencies of 299.78 and 75.38 MHz for \(^1\)H and \(^13\)C, respectively. \(^1\)H MAS experiments were carried out with a π/2 pulse width of 5.0 μs and a repetition time of 2 s. \(^13\)C MAS experiments with \(^1\)H decoupling were performed by using a π/2 pulse width of 5.5 μs and a repetition time of 2 s. The magic angle spinning rate was set to 3.5 KHz. The chemical shifts of \(^1\)H and \(^13\)C were referenced to adamantane (1.99 ppm for \(^1\)H, 29.9 ppm for \(^13\)C-methyl, and 39.0 ppm for \(^13\)C-methylene).

ESR experiments were carried out at the X-band using a JEOL FA 2000 spectrometer. The microwave frequency was 9.1 GHz, the modulation amplitude was 0.1 mT, the microwave power was 5 mW, and the experimental temperature was 295 K. The G values of the radical species were referenced to a Mn marker.
3. RESULTS AND DISCUSSION

3.1. Surface Hydroxyl Groups and Adsorbed H2O on Pt/TiO2 Catalysts Studied by Solid-State 1H MAS NMR.

To clarify the structure and distribution of Ti—OH groups and adsorbed H2O on the surface of Pt/TiO2 catalysts, 1D and 2D 1H solid-state MAS NMR techniques were utilized. Figure 1a shows the 1D 1H MAS NMR spectrum of the Pt/TiO2 catalyst (PT-1) dehydrated at 473 K. It can be seen that two types of surface hydroxyl groups are present, consistent with previous reports.13−16 The signals at 1.8 and 7.3 ppm can be assigned to terminal hydroxyl groups (OH T) and bridging hydroxyl groups (OH B), respectively, while the sharp signal at 0 ppm is due to the small amount of impurities (silicone grease, amounts to ca. 2.8% of the total proton content, Figure S1 in the Supporting Information). For the Pt/TiO2 catalyst (PT-2) dehydrated at 673 K, the OH T groups are predominant on the surface of TiO2, while the OH B groups are largely diminished (Figure 1b), indicating that the OH B groups are preferentially removed by the high-temperature dehydration. By careful spectral deconvolution, we found that when additional H2O is absorbed onto the PT-2 sample, the OH B groups (7.3 ppm) are gradually recovered (Figure 1c,d), while the amount of OH T groups remains almost constant with increasing H2O loadings (Figure 1e–h). A similar trend is observable for PT-1 with the H2O loading being increased from 0.2 to 2.7 μmol (Figure S2 in the Supporting Information).

To study the dynamics of different 1H species (OH T, OH B, and adsorbed H2O) in the Pt/TiO2 photocatalysts, we have measured their spin−spin relaxation time (T 2). Figure 3 shows the change of T 2 values for the different 1H species in the PT-1 sample as a function of the H2O loading. When the H2O loading is low, the three 1H species have similar T 2 values. With the increase of the H2O loading, the T 2 values of both adsorbed H2O and OH B considerably decrease, while that of OH T slightly declines. Generally, a smaller T 2 value should indicate a weaker mobility, and vice versa. Thus, the proton mobility of both adsorbed H2O and OH B is largely reduced with the H2O appears, and it grows gradually with the increase of the H2O loadings (Figure 1e–h). A similar trend is observable for PT-1 with the H2O loading being increased from 0.2 to 2.7 μmol (Figure S2 in the Supporting Information).

2D 1H−1H DQ MAS NMR spectroscopy is a powerful method for probing proton−proton proximities/interactions in various solid materials31−34 and was employed here to investigate the spatial proximities of various Ti−OH groups and the adsorbed H2O. The presence of a signal in the 1H−1H DQ MAS NMR spectrum indicates that two protons are in close proximity (<5 Å), as the DQ coherences observed are strongly dependent on the internuclear distance. Peaks that occur along the diagonal (ω1, 2ω1) are autocorrelation peaks resulting from the dipolar interaction of protons with the same chemical shift, while pairs of off-diagonal peaks at (ω1, ω2 + ω4) and (ω2, ω2 + ω6) correspond to correlations between two protons with different chemical shifts. As shown in Figure 2a, the 2D 1H−1H DQ MAS NMR spectrum of PT-2 shows only one diagonal peak at (1.8, 3.6) ppm due to the autocorrelation of OH T groups, indicating that they are in close spatial proximity to each other. For PT-2 with a 0.9 μmol H2O loading, two diagonal peaks at (1.8, 3.6) and (7.3, 14.6) ppm are observable (Figure 2b), corresponding to the autocorrelations of OH T and OH B groups, respectively. This suggests that the OH T groups are only in close spatial proximity to other OH T groups, and the OH B groups are also only in close spatial proximity to other OH B groups. The possible reason is that the two different types of Ti—OH groups may be present on different crystal planes of TiO2. After 1.1 μmol of H2O is introduced onto PT-2, four autocorrelation peaks can be identified in the 1H−1H DQ MAS spectrum of PT-2 (Figure 2c). Again, the autocorrelation peaks at (1.8, 3.6) and (7.3, 14.6) ppm correspond to the spatial proximity of OH T and OH B groups, respectively. The new autocorrelation peak at (5.2, 10.4) ppm can be ascribed to the spatial proximity of the hydrogen atom of adsorbed H2O. Another new autocorrelation peak appears at (6.9, 13.8) ppm, and it grows with the consumption of the autocorrelation peak at (7.3, 14.6) ppm when the H2O loading is gradually increased from 1.1 to 3.6 μmol (Figure 2c–f). As such, the signal at 6.9 ppm can be assigned to the 1H signal of the OH B group in hydrogen-bonding interaction with surface-adsorbed H2O. Besides the autocorrelation peaks, an intense off-diagonal peak pair at (5.2, 12.1) and (6.9, 12.1) ppm is observable as well, corresponding to the spatial correlation between the surface-adsorbed H2O and the bridging hydroxyl (OH B) groups. It is interesting to note that even when the amount of adsorbed H2O exceeds that of OH B groups (1.8 μmol), the surface-adsorbed H2O is only correlated to OH B groups rather than OH T groups (Figure 2e). All these findings indicate that surface H2O only adsorbs on OH B groups through hydrogen-bonding interaction, forming hydrated OH B groups, which is crucial to the photocatalytic reaction (see below).

To study the dynamics of different 1H species (OH T, OH B, and adsorbed H2O) in the Pt/TiO2 photocatalysts, we have measured their spin−spin relaxation time (T 2). Figure 3 shows the change of T 2 values for the different 1H species in the PT-1 sample as a function of the H2O loading. When the H2O loading is low, the three 1H species have similar T 2 values. With the increase of the H2O loading, the T 2 values of both adsorbed H2O and OH B considerably decrease, while that of OH T slightly declines. Generally, a smaller T 2 value should indicate a weaker mobility, and vice versa. Thus, the proton mobility of both adsorbed H2O and OH B is largely reduced with the
increase of the H$_2$O loading as compared to OH$_T$, which could be ascribed to the interaction between adsorbed H$_2$O and OH$_T$. This result suggests that, with respect to OH$_B$, the OH$_T$ should be present in a different chemical environment in which the interaction between OH$_T$ and H$_2$O is very weak. A similar result can also be derived from the 2D $^1$H−$^1$H NOESY correlation NMR spectra acquired with different mixing times for hydrated PT-1 (Figure S3 in the Supporting Information).

As shown in Figure S3, at a short mixing time (10 ms), the correlation between OH$_B$ and H$_2$O is observable, while the correlations between OH$_T$ and OH$_B$/H$_2$O are absent, which is consistent with the $^1$H−$^1$H DQ experimental result. At a long mixing time (80 ms), the correlations between OH$_T$ and OH$_B$/H$_2$O appear, implying that only long-range/weak interactions are present between OH$_T$ and OH$_B$/H$_2$O.
3.2. Structure–Activity Relationship of Ti–OH and Adsorbed H2O Studied by In Situ NMR Techniques. The photocatalytic hydrogen production processes from coadsorption of water and methanol on Pt/TiO2 catalysts were characterized as functions of the irradiation time and H2O loadings by in situ 13C and 1H solid-state MAS NMR techniques. Figure 4 shows the typical in situ 13C and 1H MAS NMR spectra of PT-1 photocatalysts coadsorbed with 3.0 μmol of 13CH3OH and 2.7 μmol of H2O as a function of the irradiation time ranging from 0 to 240 min. At 30 min of irradiation, in addition to the signal of unreacted 13CH3OH at 49.0 ppm, two weak signals appear at 54.4 and 91.4 ppm, which can be assigned to dimethoxymethane (derived from the acetalization of HCHO and CH3OH). The oxidation of CH3OH proceeds with the irradiation time being increased to 60 min, which is evidenced by the increase of dimethoxy methane and the appearance of carbon dioxide (δ = 125.9 ppm) and formic acid (δ = 173.1 ppm). Further prolonging the irradiation time from 60 to 240 min leads to an increase of carbon dioxide at the expense of methanol, dimethoxymethane, and formic acid. It can be deduced that methanol is successively photo-oxidized to form dimethoxymethane, formic acid, and carbon dioxide, which is consistent with the previous reports. On the other hand, in situ 1H MAS NMR spectra (Figure 4, right) were recorded to detect the H2 production as a function of the irradiation time, in which the strong broad signal at 5.9 ppm can be assigned to the fast proton exchange among surface-hydrated OHB, adsorbed H2O, and the hydroxyl of CH3OH, the signals at 3.8 and 3.5 ppm are due to the J-coupling peaks of 1H–13C in the methyl group of CH3OH, and the signal at 1.8 ppm is due to the surface OHF group. When the irradiation time is increased to 30 min, the production of H2 (δ = 4.4 ppm) is evident, and the amount of H2 gradually increases with the consumption of the protons of H2O, OHB, and CH3OH with further increasing the irradiation time.

The photocatalytic reaction processes on both PT-1 and PT-2 photocatalysts with different Ti–OH groups and variable H2O loadings were thoroughly studied by in situ 13C and 1H NMR techniques (see Figures S4 and S5 in the Supporting Information). On the basis of the in situ NMR results, the evolution of the apparent rate constant of photocatalytic H2 production (determined by calculating the integral area of the 1H NMR signal of H2 as a function of the solar-light irradiation time) as a function of the H2O loading over PT-1 and PT-2 photocatalysts was ascertained (Figure 5a). It can be found that the photocatalytic activity of PT-1, on which both OHB and OHF groups are present, is negligible in the absence of adsorbed H2O, implying that the presence of CH3OH and Ti–OH on the surface of TiO2 does not result in the transfer of the...
photoinduced hole to adsorbed molecules. The photocatalytic activity is dramatically enhanced when the amount of adsorbed H₂O is increased from 0 to 1.8 μmol. When the amount of adsorbed H₂O is ca. 1.8 μmol, which is equal to the amount of surface OH₅ groups, the photocatalytic activity reaches a maximum, while it slightly declines with further increasing the H₂O loading. This indicates that the innermost adsorbed H₂O molecules (such as those adsorbed on the OH₅ groups through hydrogen bonds) should be crucial to the photocatalytic reaction, and have a significant impact on the photocatalytic activity. Compared with PT-1, the PT-2 photocatalyst, which mainly retains OH₅ groups, exhibits a different evolution trend for the apparent rate constant as a function of the H₂O loading. The photocatalytic activity of PT-2 is slightly improved with the increase of the H₂O loading in the range of 0–0.9 μmol. Obviously, an “induction period” for the formation of surface active centers is present, during which the OH₅ groups (with the ¹H chemical shift at 7.3 ppm; see Figure 1b,c,d) are regenerated due to the reaction of adsorbed H₂O molecules with oxygen vacancies. With further increasing the H₂O loading, the evolution trend of the photocatalytic activity of PT-2 is similar to that of PT-1. Obviously, the existence of OH₅ groups is an essential prerequisite to the photocatalytic reaction. In addition, as revealed by our ¹H MAS NMR results, the surface H₂O adsorbs solely on the OH₅ groups through hydrogen bonds to form hydrated OH₅ groups. Thus, the correlation between the amount of hydrated OH₅ groups and the photocatalytic activity was also established and is shown in Figure 5b. It can be seen that the photocatalytic activity is almost linearly enhanced with the increase of the hydrated OH₅ content, and it reaches a maximum when the amount of hydrated OH₅ groups increases to 1.8 μmol. With further increasing the H₂O loading, the amount of hydrated OH₅ remains constant, and the photocatalytic activity does not increase but slightly declines (Figure 5a). Therefore, we can conclude that the hydrated OH₅ group is essential to the photocatalytic reaction and should be the photocatalytically active site.

3.3. Active Paramagnetic Intermediates Studied by In Situ ESR. To gain insight into the role of hydrated OH₅ groups in the photoinduced hole-transfer process, in situ ESR experiments were performed before and after 30 min of solar-light irradiation on the PT-1 catalysts with different H₂O loadings, and the results are shown in Figure 6. For the bare PT-1 sample, only a weak signal with a g value of 1.9996 due to a small amount of oxygen defects is visible before solar-light irradiation (Figure 6a, black line). This signal remains almost unchanged upon 30 min of solar-light irradiation (Figure 6a, red line), which can be attributed to the rapid recombination of photoinduced holes and electrons. Interestingly, when a small amount of oxygen defects is visible before solar-light irradiation (Figure 6a, black line). This signal remains almost linearly enhanced with the increase of the hydrated OH₅ content, and it reaches a maximum when the amount of hydrated OH₅ groups increases to 1.8 μmol. With further increasing the H₂O loading, the amount of hydrated OH₅ remains constant, and the photocatalytic activity does not increase but slightly declines (Figure 5a). Therefore, we can conclude that the hydrated OH₅ group is essential to the photocatalytic reaction and should be the photocatalytically active site.

When the H₂O loading is increased to 1.1 μmol (the amount of hydrated OH₅ groups is 1.1 μmol), new ESR signals with g = 2.000–2.021 are visible upon solar-light irradiation (Figure 6c, red line), indicative of the formation of new surface paramagnetic species. According to previous reports, the ESR signals of orthorhombic symmetry at gzz = 2.021, gsx = 2.008, and gxy = 2.000 could be ascribed to surface superoxide Tiₕ−O₂⁻− sites. The O₂⁻− anion is usually stabilized on a metallic cationic site so that the electrostatic interaction splits the 2π* antibonding orbitals by an amount (δ) due to the local cationic crystal field. The gzz value can be measured by the equation gzz = gₑ + 2λ/δ, where λ is the spin–orbit coupling constant of oxygen. The gzz value of 2.021 indicates that the O₂⁻− is stabilized at the Ti⁴⁺ cation. To have a more detailed analysis, spectral simulations were performed. As shown in Figure 6j, the sum of the simulated spectra of surface Ti−O⁻− (Figure 6g) and Ti−O₂⁻− (Figure 6h) paramagnetic centers could well reproduce the experimental spectrum (Figure 6c) of PT-1 with a 1.1 μmol H₂O loading. Furthermore, to detect the stability of Ti−O⁻− and Ti−O₂⁻− centers, the evolution of ESR signals of the hydrated PT-1 sample as a function of the dark time was monitored by the in situ ESR technique (Figure 7a). By spectral simulation, we find that, with the increase of the dark time, the signal of Ti−O⁻− gradually disappears, while only the orthorhombic signal of Ti−O₂⁻− still exists even after 24 h.

When the H₂O loading is raised to 1.8 μmol, the content of hydrated OH₅ groups reaches maximum (1.8 μmol). Only the

![Figure 6. In situ ESR spectra (left) of PT-1 before (black line) and after (red line) 30 min of solar-light irradiation with different H₂O loadings: (a) 0 μmol, (b) 0.2 μmol, (c) 1.1 μmol, (d) 1.8 μmol, (e) 2.7 μmol, and (f) 3.6 μmol. Simulated spectra (right) of (g) Ti−O⁻−, (h) Ti−O₂⁻−, (i) Pt−O₂⁻−. (j) PT-1 loaded with 1.1 μmol of H₂O (the corresponding experimental spectrum is that in (c)), and (k) PT-1 loaded with 2.7 μmol of H₂O (the corresponding experimental spectrum is that in (e)).](image-url)
broad orthorhombic ESR signal ($g_{zz}$ = 2.021, $g_{yy}$ = 2.008, and $g_{xx}$ = 2.000) of Ti$^{-}$O$^{2-}$ is present and reaches a maximum, while the signal of Ti$^{-}$O$^{-}$ completely disappears upon solar-light irradiation (see parts d, red line, and h of Figure 6). Thus, with the increase of the hydrated OH$_B$ content, the active paramagnetic intermediate is converted from Ti$^{-}$O$^{-}$ to Ti$^{-}$O$^{2-}$ (the valence of the oxygen atom changes from $-1$ to $-1/2$). This indicates that increasing the trapping and transfer of photoinduced holes on the hydrated OH$_B$ groups should be crucial for improving the activity of photocatalytic water splitting.

With further increasing the H$_2$O loading to 2.7 $\mu$mol, the amount of hydrated OH$_B$ groups remains unchanged. In this case, the ESR signals (Figure 6e, red line) for active paramagnetic intermediates could be deconvoluted by two different components (Figure 6k): one corresponds to the residual Ti$^{-}$O$^{2-}$ site, and the other with $g_{zz}$ = 2.022, $g_{yy}$ = 2.007, and $g_{xx}$ = 2.001 (Figure 6i) is a typical ESR signal of weakly absorbed O$_2^{-}$ species which is usually generated by the reduction of O$_2$ on metal-loaded zeolite catalysts. Here we assign the signals with $g_{zz}$ = 2.022, $g_{yy}$ = 2.007, and $g_{xx}$ = 2.001 to the weakly absorbed superoxide (Pt$^{-}$O$_2^{-}$) arising from the reduction of O$_2$ by photoinduced electrons on the cocatalyst Pt.

Therefore, when the amount of adsorbed H$_2$O exceeds that of saturation adsorption on the OH$_B$ groups, the Ti$^{-}$O$^{2-}$ center will be further oxidized to generate O$_2$ by the photoinduced hole. Part of the O$_2$ molecules interact with the cocatalyst Pt and then are reduced to form the weakly absorbed O$_2^{-}$ species by photoinduced electrons, which should be responsible for the decrease of the ESR signal of active paramagnetic intermediates. Of course, the formed O$_2$ molecules can readily trap the photoinduced electron to regenerate Ti$^{-}$O$^{2-}$ species as well on the surface of TiO$_2$ as previously reported. The evolution of the ESR signals of the hydrated PT-1 photocatalyst as a function of the dark time was also studied by the in situ ESR technique. As shown in Figure 7b, only the orthorhombic signal of Ti$^{-}$O$^{2-}$ is detectable after 24 h.

When the H$_2$O loading is increased to 3.6 $\mu$mol, only the narrow orthorhombic ESR signals of weakly adsorbed O$_2^{-}$ species ($g_{zz}$ = 2.022, $g_{yy}$ = 2.007, and $g_{xx}$ = 2.001) are observable upon solar-light irradiation (parts f, red line, and i of Figure 6). Although part of the O$_2$ molecules are consumed to trap the photoinduced electrons on the cocatalyst Pt, forming the Pt$^{-}$O$_2^{-}$ intermediate, the total amount of active paramagnetic intermediates decreased obviously, which should be responsible for the declined activity of photocatalytic water splitting. To validate the activity of these paramagnetic intermediates (Ti$^{-}$O$^{-}$, Ti$^{-}$O$^{2-}$, and Pt$^{-}$O$_2^{-}$), a small amount of methanol (ca. 0.5 $\mu$mol) was introduced onto the various hydrated PT-1 samples. It could be found that their ESR signals disappear completely upon solar-light irradiation (Figure S6 in the Supporting Information), and simultaneous oxidation of methanol occurs, indicating that all these paramagnetic intermediates possess high oxidation activity. Therefore, all these experimental results confirm that the hydrated OH$_B$ group is the transfer channel of the photoinduced hole.
which controls the oxidation of both adsorbed H₂O and organic compounds on the TiO₂ surface.

3.4. Photocatalytic Mechanism. Hydrogen production (reduction of H⁺ by photoinduced electron) proceeds on the Pt cocatalyst in this case, while the oxidation of the photoinduced hole is characterized by the formation of active radicals on the surface active sites of TiO₂ for oxidation of water and organic compounds. The above NMR and ESR experimental results allow us to propose the hole-transfer mechanism for photocatalytic water splitting on the TiO₂ photocatalyst upon solar-light irradiation, as illustrated in Scheme 1. According to our NMR and ESR experimental results, it can be concluded that the hydrated OHB groups are the photocatalytic active sites to trap the photoinduced holes, which trigger the oxidation of water and organic compound. Theoretical results also suggested that the mismatch between the valence band of TiO₂ and the O 2p levels of Ti–OH groups and adsorbed H₂O could be overcome by the overpotential created by the photoinduced hole in the vicinity of Ti–OH groups. As shown in Scheme 1, upon solar-light irradiation, the hydrated OHB groups trap a photoinduced hole to generate the Ti−O⁻ intermediate associated with the ESR signal at \( g_∥ = 2.020 \) and \( g_τ = 1.999 \). Meanwhile, a nucleophilic attack of adsorbed H₂O to the hole-trapped sites occurs, which hinders the recombination of photoinduced electrons and holes (i.e., the recombination of Ti−O⁻ with the adjacent Ti sites), and thereby stabilizes the formation of Ti−O⁻ species. It is noteworthy that when the amount of adsorbed H₂O is low on the TiO₂ surface, only an isolated hydrated OHB group is present, and thus, only the Ti−O⁻ species is formed and stabilized under solar-light irradiation. With the increase of the amount of adsorbed H₂O, the hydrated OHB groups increase gradually and are adjacent to each other. When another photoinduced hole is trapped by a neighboring hydrated OHB group and the hole-trapped site is nucleophilically attacked by another adsorbed H₂O, two adjacent Ti−O⁻ centers can couple with each other to form surface peroxide species as shown in Scheme 1. It was previously reported that the H₂O₂ could react with TiO₂ powder, forming surface O₂⁻ species.\(^{18}\) As such, the surface peroxide intermediate would be oxidized by the photoinduced hole to form Ti−O₂⁻ species associated with the ESR signals with \( g_∥ = 2.021 \) and \( g_τ = 2.008 \), and \( g_τ = 2.000 \). Meanwhile, the nucleophilic attack of an adjacent OHB group on the Ti atom leads to the recovery of OHB group, which favors the formation and stabilization of the Ti−O₂⁻ center. A further oxidation of the Ti−O₂⁻ center by the photoinduced hole results in the formation of an O₂ molecule followed by the recovery of another OHB group arising from the nucleophilic attack of an adjacent OHB group. The excessive H₂O molecules adsorb on the regenerated OHB groups, which may hinder the interaction between the O₂ molecule and the TiO₂ surface, and further prevent the O₂ molecule from trapping the photoinduced electron to form Ti−O₂⁻ species. Then the O₂ molecule would interact with the cocatalyst Pt and be reduced to form Pt−O₂⁻ species by the photoinduced electron. This is consistent with our experimental observation that when the amount of adsorbed H₂O exceeds the saturation adsorption capacity of OHB groups, the ESR signal of Pt−O₂⁻ begins to appear as shown in Figure 6e,f.\(^{19,20}\) Actually, the Pt−O₂⁻ species were usually assumed to be the active radicals for oxidation of organic compounds in actual photocatalytic reactions of the TiO₂ system with massive H₂O molecules.\(^{19,20}\) As such, the O₂⁻ species can be consumed by the sacrificial reagent (methanol) to hinder the consumption of photoinduced electrons, while the reduction of O₂⁻ species by the photoinduced electron (\( O_2^- + 2H^+ + e \rightarrow H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O \)) should be responsible for the low efficiency of the photocatalytic pure water splitting. On the other hand, the reduction of H⁺ arising from OHB groups and adsorbed H₂O by photoinduced electrons on the cocatalyst Pt produces the H₂ molecule.

4. CONCLUSIONS

In summary, the surface active sites and the photocatalytic mechanism of water splitting on the surface of Pt/TiO₂ catalysts have been investigated by solid-state NMR and in situ ESR techniques. Our experimental results unambiguously demonstrated that the hydrated OHB groups were the surface active sites during photocatalytic water splitting, and the quantitative correlation between the amount of hydrated OHB groups and the photoactivity of water splitting was established for the first time. The evolution of paramagnetic active intermediates on the TiO₂ surface with different amounts of surface-adsorbed H₂O under solar-light irradiation was monitored by in situ ESR spectroscopy, which revealed that the hydrated OHB groups offer a channel for the transfer of the photogenerated hole in the photocatalytic reaction. On the basis of the experimental observations, we proposed the detailed hole-transfer mechanism for photocatalytic water splitting on the TiO₂ photocatalyst. The results presented herein should not only facilitate a better understanding of the photocatalytic mechanism at the atomic level but also be helpful for the rational design of highly active titania-based photocatalysts.

ASSOCIATED CONTENT

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.7b04877.

Spectral deconvolution of the \(^1H\) MAS NMR spectrum of PT-1, \(^1H\) MAS spectra of PT-1 with various H₂O loadings, 2D \(^3H\)−\(^1H\) NOESY correlation NMR spectra of hydrated PT-1 acquired with different mixing times, in situ \(^13C\) and \(^1H\) MAS NMR spectra of the photocatalytic reaction on PT-1 and PT-2 photocatalysts with different Ti−OH groups and variable H₂O loadings, and in situ ESR spectra before and after 0.5 μmol of methanol being introduced to PT-1 with different H₂O loadings (PDF)

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Notes
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