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RESEARCH NOTE

UV-Enhanced Exchange of O_2 with H_2O Adsorbed on TiO_2

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Ultraviolet light dramatically increases the rate of isotope exchange between gas-phase O_2 and water adsorbed on TiO_2 at room temperature, but it does not affect the rate of CO_2–water exchange. Both ethanol and acetaldehyde, when coadsorbed with $H_2{}^{18}O$, dramatically decrease the rate of O_2 exchange, but not CO_2 exchange, with adsorbed $H_2{}^{18}O$. This decrease is attributed to a combination of competition for adsorbed oxygen between exchange and photocatalytic oxidation of the adsorbed organic and blocking of the oxygen adsorption sites by the organic. The same oxygen species participate in O_2-$H_2{}^{18}O$ exchange and photocatalytic oxidation. © 1999 Academic Press

INTRODUCTION

Heterogeneous photocatalytic oxidation (PCO) has potential applications for complete oxidation of organic pollutants in dilute systems. Organics can be oxidized to CO_2 and H_2O at room temperature on TiO_2 catalysts in the presence of UV or near-UV illumination. The UV light excites electrons from the valence to the conduction band of the semiconductor catalyst, leaving holes behind. The electron–hole pairs can initiate redox reactions with surface species.

The roles of O_2 and water during PCO are not well understood. Some studies have reported that photocatalytic activity decreases in the absence of water in the feed stream (1–4), whereas higher water concentrations can have an inhibitory effect (1, 3). In other studies (5–8) with various reactants, PCO took place in a dry feed stream without deactivation. We showed previously (5) that, although high water concentrations reduce the surface coverages of ethanol and its intermediates, the rate of CO_2 formation did not change. Lu *et al.* (9), using isotopically labeled O_2 and water, observed that oxygen from adsorbed $H_2{}^{18}O$ was incorporated into some reaction products during PCO of CH_3Cl. They concluded that water participates in PCO when adsorbed oxygen is present, and thus the rate of exchange between O_2 and H_2O is of interest for better understanding PCO. We studied the effect of UV irradiation on O_2 and CO_2 exchange with absorbed $H_2{}^{18}O$ on TiO_2 and the effect of co-adsorbed organics on the exchange rate.

Ultraviolet light has been reported to increase the exchange between gas-phase O_2 and the lattice oxygen of TiO_2 at room temperature (10, 11). Courbon *et al.* (11) determined that both UV light and TiO_2 are required for oxygen isotope exchange and proposed an exchange mechanism that involved one surface oxygen atom at a time. They correlated the oxygen isotope exchange rate with the PCO rate of isobutane to acetone. During PCO of isobutane in a batch reactor with excess $^{18}O_2$, oxygen isotope exchange took place only after the all the isobutane had reacted, even though the isobutane charge corresponded to a coverage of only 10^{-2} isobutane molecules/nm^2. They concluded that the same surface oxygen species participates in PCO and oxygen exchange.

In contrast, when Yanagisawa and Ota (12) adsorbed $^{18}O_2$ at 90 K on rutile TiO_2, oxygen did not exchange with the surface when it was irradiated by UV at room temperature, although they observed $^{18}O_2$ photodesorption. Yanagisawa *et al.* (13) used TPD to determine the extent of isotope exchange between adsorbed O_2 and a MgO surface that had been *previously* irradiated by UV light. They exposed the MgO surface to UV light for 10 min at room temperature before cooling to 80 K and adsorbing $^{18}O_2$. During the subsequent TPD, they observed $^{16}O^{18}O$ peaks.

EXPERIMENTAL METHODS

The apparatus used for photocatalytic exchange and TPD was described previously (14). Approximately 30 mg of Degussa P-25 TiO_2 catalyst was coated as a thin layer (average thickness <0.5 μm) on the inside of an annular Pyrex reactor so that all the TiO_2 was exposed to UV light. The annular reactor had a 1-mm annular spacing so that high gas flow rates could be maintained across the catalyst to minimize mass transfer effects and rapidly flush gas phase products from the reactor. The outside diameter of the reactor was 2 cm and the reactor was 13 cm high so that sufficient catalyst mass was present to allow detection of the reaction

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products by the mass spectrometer. Six UV lamps (GE, 4 W) surrounded the photocatalytic reactor and the light intensity at the catalyst surface location, measured with a radiometer, was approximately 0.3 mW/cm^2. The radiometer could only measure light from one direction, but the light that penetrated through the thin catalyst layer would strike the layer on the other side of the reactor and, thus, the intensity was greater than 0.3 mW/m^2. This made the intensity variation at different locations around the reactor less, but the light was more intense at the midpoint of the reactor than at the ends. The maximum light intensity was near 360 nm (15).

Before each experiment, heating the reactor for 30 min in approximately 20% O_2 in He to 723 K and then cooling to room temperature created a reproducible surface. Metal shields were placed between the reactor and the UV lights, and the shields were removed to illuminate the catalyst after the lights attained a steady-state output. Two 1-μL pulses of $H_2{}^{18}O$ (Isotec, 99% ^{18}O enrichment) saturated the catalyst in the dark prior to exchange. Exchange was studied by injecting $^{16}O_2$ (560 μmol/g catalyst) and $C^{16}O_2$ (220 μmol/g catalyst) pulses or by continuously flowing 0.2, or 3% O_2 in He over a monolayer of $H_2{}^{18}O$ adsorbed on the catalyst. The exchange was studied both in the dark and under UV illumination.

The exchange of O_2 and CO_2 with $H_2{}^{18}O$ that was coadsorbed with ethanol or acetaldehyde was also studied. During the O_2 exchange, the adsorbed organic was oxidized photocatalytically. Either a monolayer of organic (ethanol or acetaldehyde) was adsorbed and then two pulses of $H_2{}^{18}O$ (560 μmol/g catalyst) were injected upstream of the reactor or a monolayer of water was adsorbed and then two pulses of organic (560 μmol/g catalyst) were injected before UV illumination. Changing the adsorption order changed the relative coverages (5). These adsorbed species were then exposed to $^{16}O_2$ pulses (560 μmol/g catalyst). For some experiments, a 150 μmol/g catalyst pulse of either acetaldehyde or ethanol was injected into the O_2 flow during exchange of a monolayer of $H_2{}^{18}O$. The duration of the pulse was approximately 2 s for acetaldehyde and 30 s for ethanol. The duration of the ethanol pulse was longer since it was injected as a liquid and more time was needed for it to evaporate.

A Balzers QMA 125 quadrupole mass spectrometer monitored the reactor effluent immediately downstream of the reactor. The mass spectrometer was interfaced to a computer to record multiple mass peaks simultaneously. The mass spectrometer signals were calibrated by injecting known volumes of gases into the flow stream downstream of the reactor and signals were corrected for cracking in the mass spectrometer. Plots of rates versus time were generated using frequent calibration of the gas-phase products by injecting known quantities into the flow stream. To calibrate the ^{18}O species, the corresponding ^{16}O species were used. After PCO or photocatalytic exchange, TPD or TPO was performed by heating the catalyst at 1 K/s to 723 K and holding at this temperature until no desorption products were detected. A He flow gas was used for TPD, whereas a 20% O_2 in He gas mixture was used for TPO.

RESULTS AND DISCUSSION

Pulsed O_2 Exchange

Figure 1 shows the rates of formation of $^{16}O^{18}O$ and $^{18}O_2$ when 0.5-ml pulses of $^{16}O_2$ were injected over illuminated and dark TiO_2 that was saturated with $H_2{}^{18}O$. A 0.5-ml pulse of $^{16}O_2$ was also injected downstream of the catalyst for calibration. No isotopic exchange was observed in the dark since the fraction of the oxygen pulse that was $^{16}O^{18}O$ (0.39%) was equal to that of the reference calibration (0.40%) and corresponds to the natural abundance of ^{18}O, which is 0.2% of total oxygen atoms. Note that the $^{16}O^{18}O$ signal during calibration had a greater maximum than that when O_2 was pulsed over the dark catalyst. Since the calibration injection port was located closer to the mass spectrometer, less peak broadening due to axial dispersion and backmixing occurred. The areas under the curves were identical, however. In contrast, when $^{16}O_2$ was pulsed over illuminated TiO_2 that was saturated with $H_2{}^{18}O$, the oxygen atoms in $^{16}O_2$ exchanged with those in the adsorbed $H_2{}^{18}O$. Approximately 2.6% of the O_2 at the reactor exit was $^{16}O^{18}O$. Approximately 4.7% of the $^{16}O^{18}O$ exchanged further with the adsorbed water to produce $^{18}O_2$ (0.13% of the total O_2 pulse) during UV illumination. The amount of ^{18}O exchanged during the experiment corresponded to 7% of the total ^{18}O in the adsorbed $H_2{}^{18}O$. Thus, UV light increased the rate of oxygen exchange dramatically at room temperature; no measurable exchange took place in the dark.

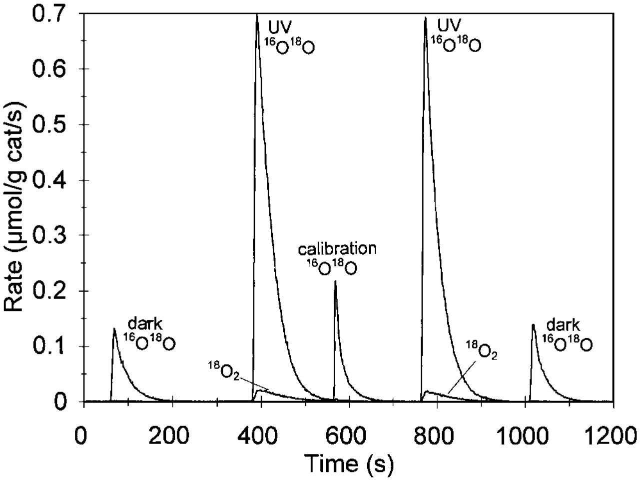

FIG. 1. Oxygen exchange between $^{16}O_2$ pulses and a monolayer of $H_2{}^{18}O$ on TiO_2 in the dark and during UV illumination.

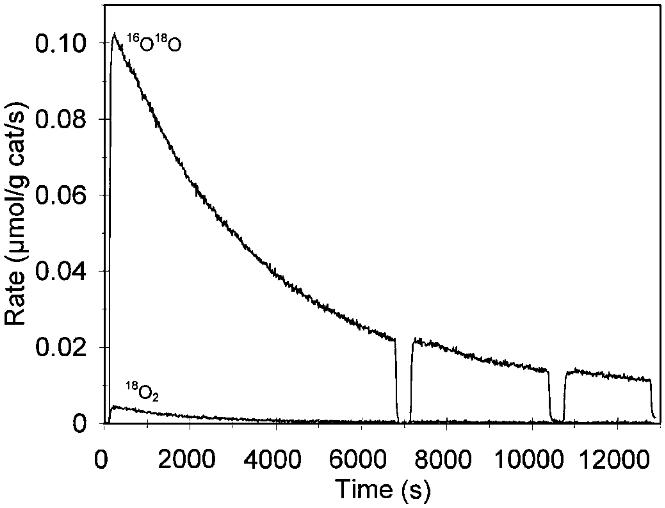

FIG. 2. Rates of formation of $^{16}O^{18}O$ and $^{18}O_2$ in 0.2% $^{16}O_2$ flow for TiO_2 under UV irradiation. The TiO_2 was saturated with $H_2{}^{18}O$ at the start of exchange.

Continuous Flow Exchange

Figure 2 shows the UV-enhanced oxygen exchange of adsorbed $H_2{}^{18}O$ with gas-phase O_2 while flowing 0.2% O_2 in He. The rates of $^{16}O^{18}O$ and $^{18}O_2$ formation quickly reach maxima and then decreased. The rate of $^{16}O^{18}O$ formation was 25 times that of $^{18}O_2$ throughout the experiment, indicating that an O_4 intermediate is not probable. This indicates that $^{18}O_2$ most likely forms from further exchange of $^{16}O^{18}O$ with adsorbed $^{18}H_2O$. In contrast, Yanagisawa *et al.* (13) presented evidence for both O_3 and O_4 intermediates for the exchange of O_2 with the lattice oxygen of MgO.

Saturation coverage of water on TiO_2 was determined previously to be approximately 750 μmol/g catalyst (16). Approximately 65% of the adsorbed $H_2{}^{18}O$ exchanged with gas-phase O_2 to form $^{16}O^{18}O$ and $^{18}O_2$ during the 3.5-h experiment, and 20% desorbed during the subsequent TPD. Water desorption was not complete when TPD was stopped, and thus approximately 15% of the adsorbed $H_2{}^{18}O$ either had not desorbed when the TPD was stopped, or it had exchanged oxygen with the surface (perhaps during TPD) and desorbed as $H_2{}^{16}O$. Exchange of oxygen between water and TiO_2 is discussed below. The rate of $^{16}O^{18}O$ formation after 3.5 h of illumination was one-tenth the initial rate, even though only 65% of the oxygen in the adsorbed $H_2{}^{18}O$ had exchanged. This may be because the light intensity was not uniform or because the TiO_2 surface is heterogeneous, with H_2O on some sites exchanging more rapidly. The lights were turned off twice for 6 min during the experiment to check for baseline drift, which was insignificant. Note that the $^{16}O^{18}O$ formation rate quickly dropped to zero when the lights were switched off, indicating that the appearance of $^{16}O^{18}O$ in the gas phase is not desorption limited.

TPD of $H_2{}^{18}O$

To determine if water and TiO_2 exchange oxygen during TPD, successive TPDs were performed by readsorbing $H_2{}^{18}O$ after each temperature ramp. The percentage of water that desorbed as $H_2{}^{18}O$ was 34% during the first TPD, 55% in the second, and 63% in the third. This suggests that a portion of the adsorbed water exchanges oxygen with TiO_2 either during TPD or at room temperature prior to TPD. The total amount of water ($H_2{}^{16}O + H_2{}^{18}O$) that desorbed during the first TPD (710 μmol/g catalyst) was similar to that reported previously (16). The amount of $H_2{}^{18}O$ that desorbed during the first TPD (250 μmol/g catalyst) was significantly less than the amount of ^{18}O detected during photocatalytic exchange and subsequent TPD of $H_2{}^{18}O$, even though the same adsorption procedure was used. This indicates that oxygen atoms in some adsorbed water molecules most likely exchange with the surface *during TPD*. The oxygen atoms in $H_2{}^{18}O$ could have exchanged at room temperature with lattice oxygens, which then exchanged with the O_2.

Pulse Exchange: Coadsorbed $H_2{}^{18}O$ and Organic

When $H_2{}^{18}O$ was coadsorbed with ethanol, pulses of $^{16}O_2$ over the UV-irradiated TiO_2 did not produce a detectable amount of $^{16}O^{18}O$ or $^{18}O_2$, even though a significant amount of $H_2{}^{18}O$ was on the surface. In contrast, the CO_2 produced by PCO readily exchanged with adsorbed $H_2{}^{18}O$. For each experiment, approximately 70% of a monolayer of organic was adsorbed. When ethanol was adsorbed first and then $H_2{}^{18}O$, 85 μmol/g catalyst of $H_2{}^{18}O$ desorbed during TPO. When the adsorption procedure was reversed, 165 μmol/g catalyst of $H_2{}^{18}O$ desorbed during TPO, compared to approximately 250 μmol/g catalyst of $H_2{}^{18}O$ that desorbed during the first TPD of a monolayer of $H_2{}^{18}O$. Water desorption was not complete when the TPD was stopped, and some adsorbed $H_2{}^{18}O$ exchanged oxygen with the surface during TPD. Similarly, when $H_2{}^{18}O$ was coadsorbed with acetaldehyde, no exchange took place when O_2 was pulsed over the UV-irradiated TiO_2 surface, and the amounts of $H_2{}^{18}O$ that desorbed during TPO were approximately the same (120–125 μmol/g catalyst) regardless of adsorption order. This result is similar to that reported by Courbon *et al.* (11); during PCO of isobutane (excess $^{18}O_2$) in a batch reactor, oxygen exchange *with lattice oxygen* took place only after the all the isobutane had reacted. Furthermore, since PCO of isobutane produces water, the absence of gas phase $^{16}O^{18}O$ or $^{18}O_2$ did not exchange with adsorbed water, although the small initial charge of isobutane would produce a small amount of water.

Continuous Flow: Organic Injection

The exchange between a monolayer of adsorbed $H_2{}^{18}O$ and flowing 0.2% O_2 immediately stopped when a

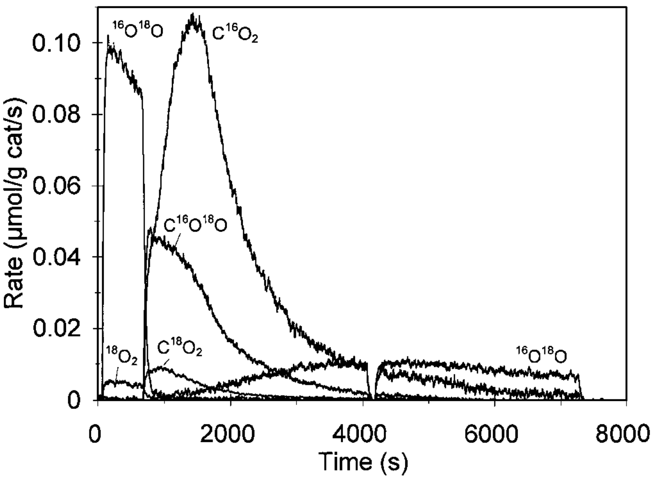

FIG. 3. Rates of formation of ^{16}O and ^{18}O-containing species on UV-illuminated TiO_2 in 0.2% O_2 flow. The TiO_2 was saturated with $H_2{}^{18}O$ at the start of the experiment. After 600 s, a pulse of ethanol (150 μmol/g catalyst) was injected.

150 μmol/g catalyst pulse of organic was injected (Fig. 3). For experiments in which either acetaldehyde or ethanol was injected, the rate of $^{16}O^{18}O$ formation immediately decreased to zero after the injection, but gradually increased after some of the organic oxidized to CO_2. The rate of $^{18}O_2$ formation also stopped when the organic was injected, but any subsequent increase in the $^{18}O_2$ rate after the organic injection could not be detected due to its low rate. Mass balances indicate that the absence of O_2 exchange was not due to complete consumption of O_2 by PCO. Approximately 15–25% of a monolayer of organic was still on the surface when the exchange between O_2 and adsorbed $H_2{}^{18}O$ resumed. These organic coverages are 50 to 100 times greater than those estimated by Courbon *et al.* (11) for their experiments with isobutane and exchange with the lattice oxygen. However, exchange with lattice oxygen may be much more sensitive to the presence of adsorbed organics, and the amount of water formed during PCO of isobutane would be small since only a small amount of isobutane was admitted into the reactor. The difference between our results and those of Courbon *et al.* suggests that $^{16}O_2$ exchange with adsorbed $H_2{}^{18}O$, and $H_2{}^{18}O$ did not first exchange with lattice oxygen, which then exchanged with $^{16}O_2$.

Note in Fig. 3 that a significant amount of the CO_2 is labeled with ^{18}O because CO_2 that formed during PCO readily exchanges with adsorbed water. Oxygen atoms readily exchanged during repeated pulses of CO_2 over adsorbed $H_2{}^{18}O$ on both illuminated and dark TiO_2. The CO_2–$H_2{}^{18}O$ exchange takes place during PCO, even though the TiO_2 has high coverages of organics (17). Illumination did not increase the rate of exchange, and thus, the exchange process for O_2 and CO_2 appear quite different. The CO_2 exchange rate was significantly greater than the UV-enhanced O_2 exchange. This may be because the CO_2 coverage is higher than the O_2 coverage on a water-saturated TiO_2 surface.

Exchange in 3% O_2

The exchange of adsorbed $H_2{}^{18}O$ with flowing 3% O_2 in He was similar to that shown in Fig. 2. Increasing the O_2 concentration from 0.2 to 3% quadrupled the maximum rate of $^{16}O^{18}O$ formation (0.42 μmol/g catalyst), but the $^{18}O_2$ maximum rate (0.01 μmol/g catalyst) was only 2.5 times that in 0.2% O_2 flow. Thus, the exchange rate was less than first order in O_2 concentration between 0.2 and 3% O_2. When the exchange was stopped after 1 h of illumination, 55% of the $H_2{}^{18}O$ monolayer had exchanged, but the rate of $^{16}O^{18}O$ formation was one-twentieth of the initial rate, due to either light nonuniformity or surface heterogeneity.

Figure 4 shows the effect of injecting ethanol (150 μmol/g catalyst) during exchange of adsorbed $H_2{}^{18}O$ in 3% $^{16}O_2$ in He flow. When ethanol was pulsed over the catalyst after 300 s of illumination, the rates of $^{16}O^{18}O$ and $^{18}O_2$ formation drastically decreased. The rate of $^{16}O^{18}O$ decreased from 0.3 to 0.02 μmol/g catalyst/s, whereas the $^{18}O_2$ rate decreased from 0.005 μmol/g catalyst/s to a rate that was approximately zero. In contrast to the results in 0.2% O_2, exchange still took place when half a monolayer of ethanol was adsorbed. This may be attributed to the change in relative rates of exchange and PCO with oxygen concentration. Increasing the O_2 concentration by a factor of 14 quadrupled the $^{16}O^{18}O$ formation rate, whereas the maximum rate of CO_2 formation in 3% O_2 (Fig. 4) only doubled. Since higher oxygen concentrations increase the rate of exchange more than the rate of PCO, exchange competes more effectively for the adsorbed oxygen.

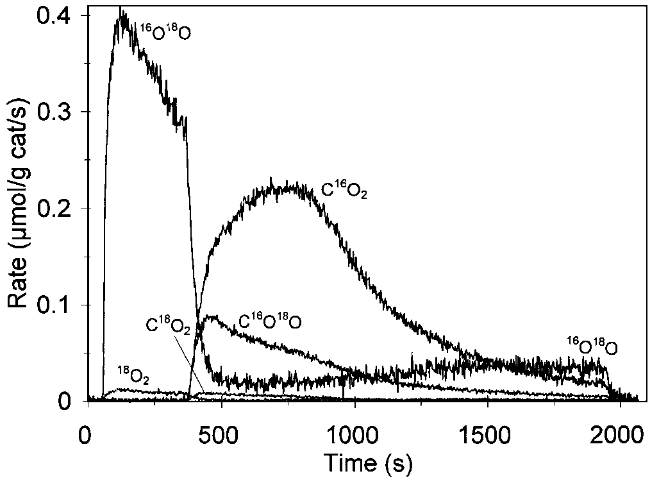

FIG. 4. Rates of formation of ^{16}O and ^{18}O-containing species on UV-illuminated TiO_2 in 3% O_2 flow. The TiO_2 was saturated with $H_2{}^{18}O$ at the start of the experiment. After 300 s, a pulse of ethanol (150 μmol/g catalyst) was injected.

Comparisons to Literature

Courbon *et al.* (11) observed that O_2 did not exchange with lattice oxygen in TiO_2 when isobutane was in the gas phase. They reasoned that PCO and exchange compete for the same oxygen intermediate, and the rate of PCO is much faster. Our results also indicate that the same oxygen species participates in PCO and O_2-$H_2{}^{18}O$ exchange. However, our initial rate of $^{16}O^{18}O$ formation due to exchange is comparable to the rate of CO_2 formation in Fig. 3. The PCO rate per adsorbed molecule is greater than the oxygen exchange rate in the absence of organics because the organic coverage is less than the water coverage and because some intermediates formed but did not desorb. Thus, the drastic drop in exchange rate is not solely due to competition with PCO for oxygen since the CO_2 formation rate during PCO is not drastically greater than the $^{16}O^{18}O$ formation rate in the absence of organics. Furthermore, Fig. 2 shows that nearly all the adsorbed $H_2{}^{18}O$ can exchange, indicating that the organic does not just displace the $H_2{}^{18}O$ that can exchange. Since the adsorbed organic readily oxidizes to CO_2, as shown in Fig. 3, the organics do not completely block oxygen adsorption sites. However, if organics block a portion of sites available for oxygen adsorption, the PCO and exchange rates cannot be directly compared. The amount of adsorbed oxygen could be much smaller in the presence of the organic, but the PCO rate is still significant at this lower O_2 concentration, whereas the exchange rate is not. Therefore the intrinsic PCO rate may be much greater than the O_2-$H_2{}^{18}O$ exchange rate but blocking of oxygen adsorption sites by adsorbed organics may mask the difference.

Yanagisawa *et al.* (13) reported low-temperature exchange between adsorbed O_2 and a MgO surface when the surface was *pretreated* with UV illumination. Our results show that on TiO_2, UV light enhances the exchange between gas-phase O_2 and adsorbed water. No exchange took place when the TiO_2 was pretreated with UV light before pulsing O_2. The O_2-$H_2{}^{18}O$ exchange may be the result of a higher concentration of surface O_2 through photoadsorption (although the amount of photoadsorbed O_2 is expected to be small), or more likely, UV light increases the exchange reaction rate.

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