FTIR Study of Adsorption and Photoassisted Oxygen Isotopic Exchange of Carbon Monoxide, Carbon Dioxide, Carbonate, and Formate on TiO$_2$

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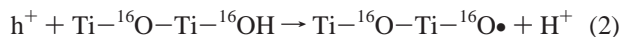
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In-situ FTIR has been employed to investigate adsorption and photoassisted oxygen scrambling of CO, CO$_2$, CO$_3$, and HCOO on powdered TiO$_2$ with $^{18}O_2$. As clean TiO$_2$ is exposed to CO at 35 °C, the IR frequencies of adsorbed CO shows that CO is bonded to Ti ions with an oxidation state +4 or less. The CO molecules that are bonded to two metal centers are more stable than those to only one center. In the case of CO$_2$ adsorption, it produces adsorbed CO$_3$ and CO$_2$ with Ti−O−C−O bonding. Adsorbed CO does not exchange oxygen with $^{18}O_2$, while adsorbed CO$_2$, CO$_3$, and HCOO do under UV irradiation. In the case of CO$_3$ with bidentate configuration, only the oxygen bonded to the carbon with carbonyl character is involved in the exchange. Possible mechanisms for the oxygen scrambling of CO$_2$, CO$_3$, and HCOO are discussed.

Introduction

Semiconductor oxides have attracted extensive studies on photocatalysis, sensor technology, and energy conversion. TiO$_2$ can photochemically induce various types of reactions which are initiated by the charge carriers (electron−hole pairs) due to TiO$_2$ excitation as it absorbs photons with energy higher than its band gap (∼3.2 eV). For the photoreactions catalyzed by TiO$_2$, O$_2$ may play important roles in photoelectron capture, forming O$_2^{•−}$ radical anions and thus increasing the lifetime of photoholes and efficiency of hole-induced surface reactions, and in participation in the subsequent reactions after the initiation step. Furthermore, O$_2$ can interact with TiO$_2$ lattice oxygen under UV-illumination as shown in eq 1.[1]

$$^{18}O_{2(g)} \xrightarrow[\text{Ti}^{16}O_2]{hv} {}^{16}O_{2(g)} + {}^{18}O^{16}O(g) \qquad (1)$$
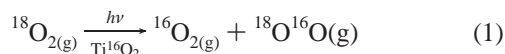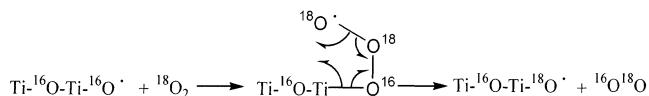
This oxygen exchange reaction is composed of sequential events. Band-gap excitation takes place to form valence-band holes and conduction-band electrons in a 10^{-15} s time scale on Ti^{16}O$_2$ UV illumination. These charge carriers are trapped on surface sites in 10^{-9} s scale following the band-gap excitation event. Electron spin resonance study has shown that, on hydrous Ti^{16}O$_2$ colloids, holes are trapped at surface hydroxyl sites to be −O$^{•−}$ radical as shown in eq 2.[2]

$$\text{h}^+ + \text{Ti}-{}^{16}\text{O}-\text{Ti}-{}^{16}\text{OH} \rightarrow \text{Ti}-{}^{16}\text{O}-\text{Ti}-{}^{16}\text{O}\bullet + \text{H}^+ \quad (2)$$

Once ^{16}O$^{•−}$ radicals are formed, the radical-philic ^{18}O$_2$ can incorporate with them. After the breakage of Ti−^{16}O and ^{18}O−^{18}O bonds and formation of a Ti−^{18}O bond, oxygen isotopic exchange is completed. Scheme 1 shows the ^{18}O and ^{16}O scrambling steps. Besides, it has been reported that O$_2$ exchanges its oxygen atom with adsorbed H$_2$^{18}O on TiO$_2$, not just TiO$_2$ lattice oxygen.[3] The subject of oxygen exchange is of importance for better understanding photocatalytic oxidation of organic molecules. We have chosen adsorbed CO, CO$_2$, CO$_3$, and HCOO as target molecules for oxygen scrambling investigation,

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SCHEME 1

based on several reasons. First, these molecules are formed as reaction intermediate or final product in photocatalytic oxidation of organics. Second, their adsorption structures on metal oxides have been extensively studied. Third, the carbon and oxygen atoms have different chemical bonding environments in these molecules which may exhibit different oxygen-scrambling reactivity.

Experimental Section

The IR cell and the sample preparation of TiO$_2$ powder supported on a tungsten fine mesh (∼6 cm^2) has been described previously.[4,5] In brief, TiO$_2$ powder (Degussa P25, ∼50 m^2/g, anatase 70%, rutile 30%) was dispersed in water/acetone solution to form a uniform mixture which was then sprayed onto a tungsten mesh. After that, the TiO$_2$ sample was mounted inside the IR cell for simultaneous photochemistry and FTIR spectroscopy. The IR cell with two CaF$_2$ windows for IR transmission down to 1000 cm^{-1} was connected to a gas manifold which was pumped by a 60 L/s turbomolecular pump with a base pressure of ∼1 × 10^{-7} Torr. The TiO$_2$ sample in the cell was heated to 450 °C under vacuum for 24 h by resistive heating. The temperature of TiO$_2$ sample was measured by a K-type thermocouple spot-welded on the tungsten mesh. Before each run of the experiment, the TiO$_2$ sample was heated to 450 °C in a vacuum for 2 h. After the heating, 10 Torr of O$_2$ was introduced into the cell as the sample was cooled to 70 °C. When the TiO$_2$ temperature reached 35 °C, the cell was evacuated for gas dosing. O$_2$ (99.998%, Matheson), CO$_2$ (99.8%, Aldrich), HCOOH (98%, Merck), and CO (99%, Aldrich) were used without further purification. Pressure was monitored with a Baratron capacitance manometer and an ion gauge. In the photochemistry study, both the UV and IR beams were set 45° to the normal of the TiO$_2$ sample. The UV light source used was a combination of a 350-W Hg arc lamp (Oriel Corp), a
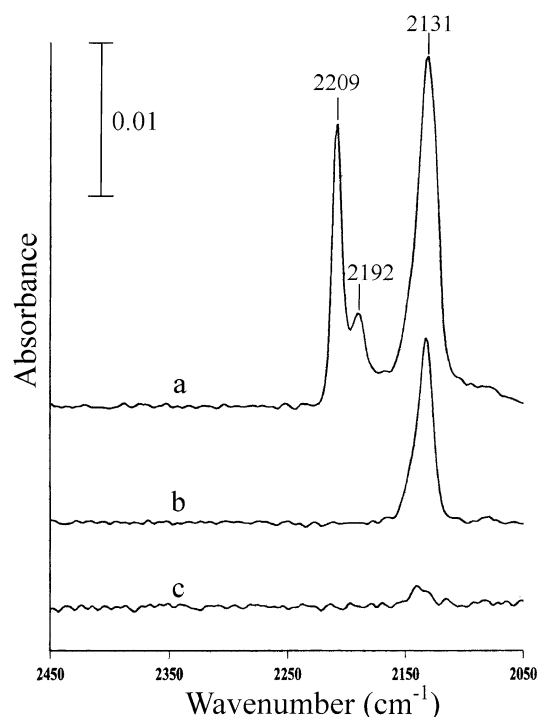
Figure 1. IR spectra for a TiO$_2$ surface in contact with 3 Torr of CO at 35 °C (a) followed by evacuation (b), and then surface heating to 70 °C in a vacuum (c).

water filter, and a band-pass filter with a bandwidth of ~100 nm centered at ~320 nm (Oriel 51650). The photon power at the position of the TiO$_2$ sample was ~0.24 W/cm^2 measured in the air by a power meter (Molectron, PM10V1). Infrared spectra were obtained with a 4 cm^{-1} resolution by a Bruker FTIR spectrometer with a MCT detector. The entire optical path was purged with CO$_2$-free dry air. The spectra presented here have been ratioed against a clean TiO$_2$ spectrum providing the metal oxide background. In the study of photooxidation, the counting of the photoirradiation time was started as the UV lamp was turned on. It took 40−50 s to reach full power.

Results and Discussion

Adsorption Study of CO, CO$_2$, CO$_3$, and HCOO. Figure 1 shows three IR spectra for a TiO$_2$ surface in equilibrium with 3 Torr of CO at 35 °C (Figure 1a) followed by evacuation at this temperature (Figure 1b) and then surface heating to 70 °C in a vacuum (Figure 1c). In the presence of gaseous CO, absorption bands appear at 2131, 2192, and 2209 cm^{-1} which are close to gaseous CO at 2143 cm^{-1} [6] and therefore are assigned to adsorbed CO on TiO$_2$. The 2131 cm^{-1} is lower than the gaseous CO frequency, while 2192 and 2209 cm^{-1} are higher, suggesting that the CO is adsorbed with different surface bonding environments. CO adsorption on a Degussa TiO$_2$ sample, with the bands at 2125, 2188, and 2208 cm^{-1}, has been studied,[5] but the 2125 cm^{-1} band which is close to our observation of 2131 cm^{-1} has not been interpreted. In Figure 1, the 2192 and 2209 cm^{-1} CO bands are removed at 35 °C under vacuum. As a contrast, the 2131 cm^{-1} band is still present at this temperature and almost disappears at 70 °C. The fact that the 2131 cm^{-1} band is more stable than the 2192 and 2209 cm^{-1} bands also reveals CO is bonded at different surface sites of TiO$_2$. CO adsorption on anatase and rutile TiO$_2$ has been studied previously.[7] The 2192 and 2209 cm^{-1} bands, are assigned to adsorbed CO bonded to Ti^{4+} ion in accordance with previous reports.[7] As CO is bonded to the metal ion without d

SCHEME 2

2192, 2209 cm^{-1} 2131 cm^{-1}, □: surface oxygen vacancy
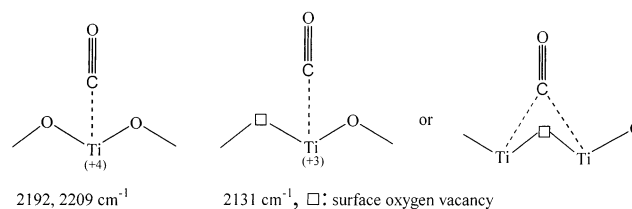
electrons, where back-donation cannot occur, its C−O stretching frequency is higher than that of CO in the gas phase. The increase of the CO frequency may result from the partial emptying of the weakly antibonding CO 5ó lone pair orbital due to its donation to the empty orbital of the metal ion.[8] On the other hand, if a coordinated CO molecule receives back-donating dπ-electrons of a metal ion into its empty 2pπ* antibonding orbital, the C−O stretching frequency tends to be decreased, compared to the gaseous CO frequency. So, as CO is adsorbed on a Ti^{3+} site on TiO$_2$, which has been detected on TiO$_2$ surface by electron spin resonance[9,10] and X-ray photoelectron spectroscopy,[11] lower C−O frequencies with respect to that of free CO molecule are expected to be observed. Previous observation of the bands at 2110−2126 cm^{-1} for CO on ZrO$_2$ has been suggested to be this type of bonding sites with reduced Zr ions.[12] Another respect for lower C−O frequency comes from metal carbonyl complexes. It is found that terminal CO usually has ~100−200 cm^{-1} larger than bridging CO which is bonded to two metal centers.[13] Since the TiO$_2$ samples used in this study possess surface oxygen vacancy sites[14] at which the Ti oxidation state is lower than +4. As CO is bonded at this site with two Ti ions, it is not surprising to observe lower C−O stretching than that of free CO. Scheme 2 shows our observed frequencies for adsorbed CO on TiO$_2$ and the proposed bonding sites.[7,12,13] Previous theoretical study of the adsorption of CO on a rutile TiO$_2$(110) surface determines that CO bonded to a 5-fold-coordinated Ti ion has a binding energy of 17 kcal mol^{-1}, while CO bonded to Ti ions at a bridging oxygen vacancy site (CO is bonded to two Ti ions in this case) has 36 kcal mol^{-1}.[15] This theoretical calculation supports our finding that the 2131 cm^{-1} band has higher stability than 2191 and 2209 cm^{-1}.
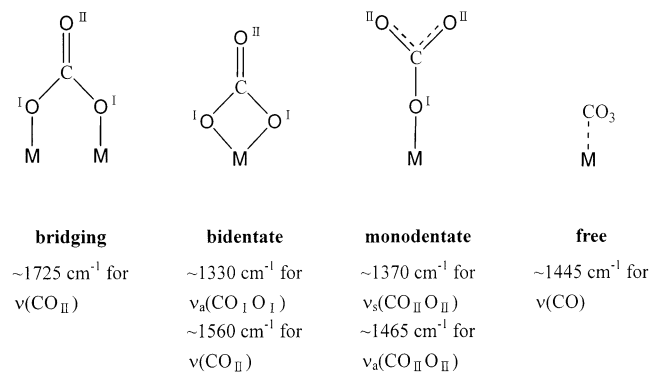
Figure 2 shows three IR spectra for a TiO$_2$ surface in equilibrium with ~0.1 Torr of CO$_2$ at 35 °C (Figure 2a), followed by evacuation (Figure 2b) and then surface heating to 70 °C in a vacuum (Figure 2c). In the presence of gaseous CO$_2$, absorption bands appear at 1319, 1376, 1462, 1532, 1579, and 2361 cm^{-1}. The 2361 cm^{-1} band is assigned to adsorbed CO$_2$ with Ti−O−C−O adsorption configuration.[16] The intensities of all of the bands are reduced under vacuum at 35 °C. After heating the surface to 70 °C in a vacuum, surface CO$_2$ is removed and the major bands left are located at 1319, 1461, and 1579 cm^{-1}. FTIR studies of adsorption of CO$_2$ on metal oxides have been reported previously.[12,13,17−23] In addition to adsorbed CO$_2$, carbonate (CO$_3$) is also produced. Scheme 3 summarizes infrared absorption frequencies and their corresponding vibrational modes of surface CO$_3$ with different bonding configurations.[12,13,17−23]

Accordingly, our observation of 1319 and 1579 cm^{-1} bands are attributed to bidentate carbonate. The 1461 cm^{-1} band may be due to monodentate carbonate or free carbonate. Based on the infrared absorption intensities, bidentate carbonate is the major species for CO$_3$ on TiO$_2$. It is interesting to compare the CO$_2$ adsorption on TiO$_2$ and ZrO$_2$. On ZrO$_2$ surface bidentate bicarbonate (HCO$_3$) has been reported to be generated upon
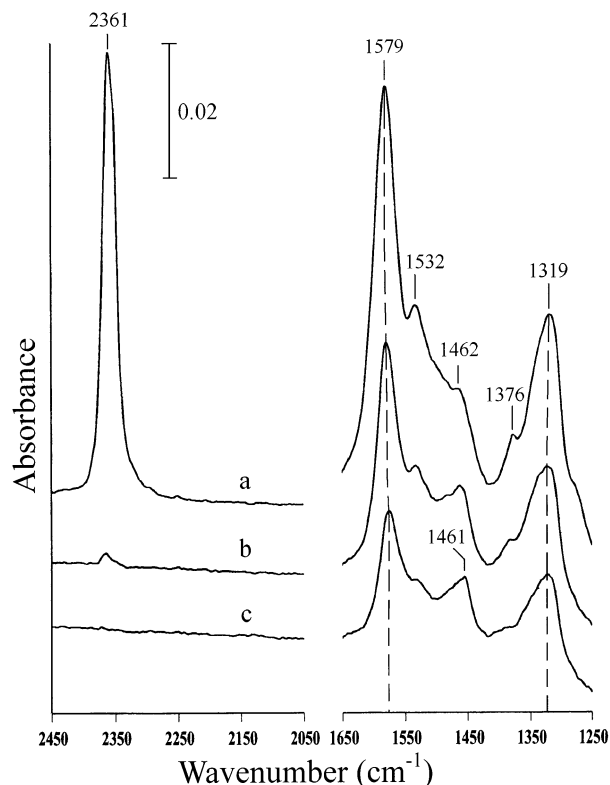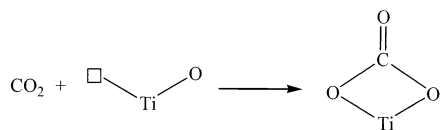
Figure 2. IR spectra for a TiO_2 surface in contact with ~0.1 Torr CO_2 at 35 °C (a) followed by evacuation (b), and then surface heating to 70 °C in a vacuum (c).

SCHEME 3

bridging	bidentate	monodentate	free
~1725 cm⁻¹ for	~1330 cm⁻¹ for	~1370 cm⁻¹ for	~1445 cm⁻¹ for
$\nu(CO_{II})$	$\nu_a(CO_I O_I)$	$\nu_s(CO_{II} O_{II})$	$\nu(CO)$
	~1560 cm⁻¹ for	~1465 cm⁻¹ for	
	$\nu(CO_{II})$	$\nu_a(CO_{II} O_{II})$	

SCHEME 4

CO_2 adsorption by the observation of IR frequencies at ~1225, ~1620, and ~3615 cm⁻¹;[12,17,19,21] however, similar bands are not found on TiO_2 in this study. Scheme 4 shows the formation of bidentate CO_3 from CO_2 adsorption on TiO_2 and the surface sites involved.

Formate (HCOO) adsorption on Degussa TiO_2 surface has been studied,[24] it exhibits absorption frequencies at ~1370 and ~1555 cm⁻¹ for symmetric and antisymmetric COO stretching and is attributed to bridging adsorption configuration. Here we focus on the oxygen mixing of adsorbed HCOO with $^{18}O_2$.
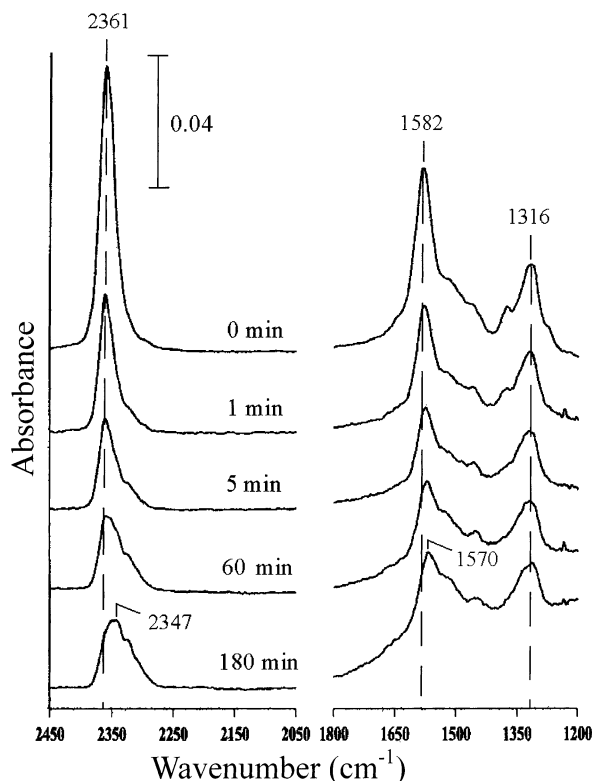
Study of Oxygen Isotopic Exchange of Adsorbed CO, CO₂, CO₃, and HCOO. Figure 3 shows the IR spectra taken before
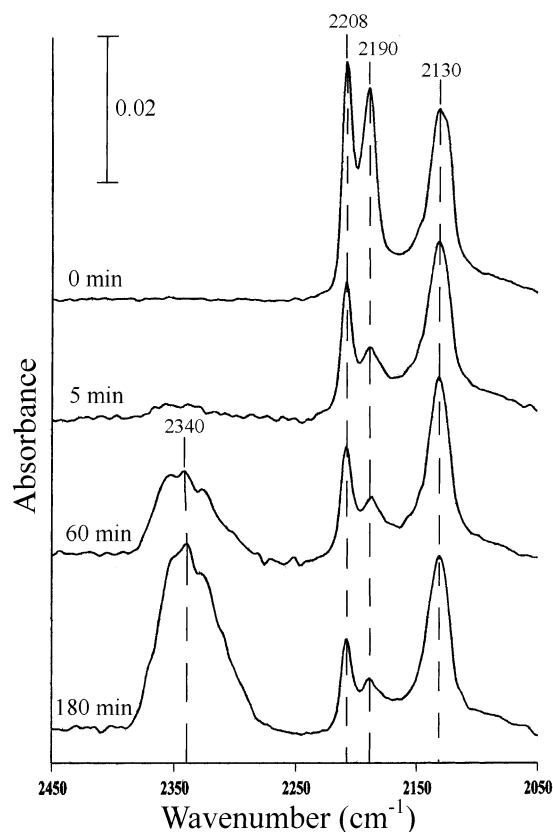
Figure 3. IR spectra taken before and after 5, 60, and 180 min during the UV exposure of a TiO_2 surface initially in a mixture of 3 Torr of CO and 10 Torr of $^{18}O_2$.
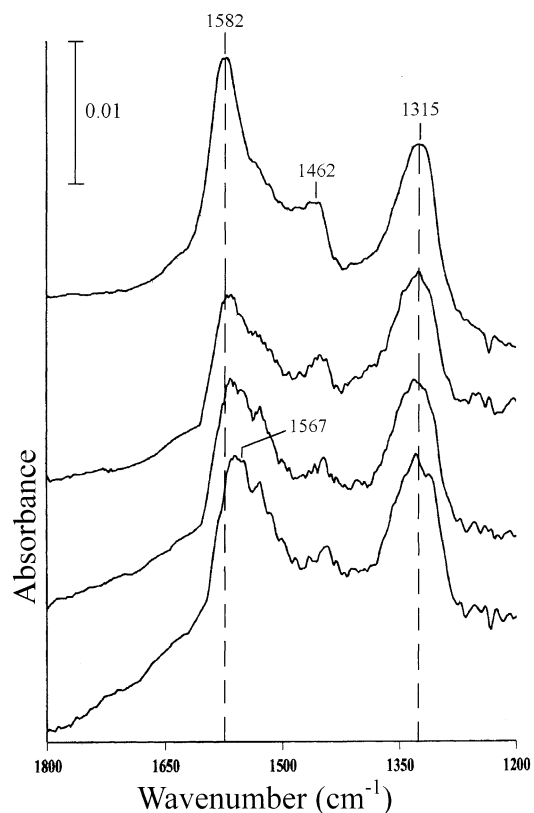
and after the indicated times during the UV irradiation of a TiO_2 surface initially in contact with a mixture of 3 Torr of CO and 10 Torr of $^{18}O_2$. Several spectral features are found during the photoillumination, including the formation of a new band at ~2340 cm⁻¹ and the decrease in intensity of the 2190 and 2208 cm⁻¹. The enhanced band at ~2340 cm⁻¹ is attributed to carbon dioxide containing ^{18}O on the basis of the IR frequencies of gaseous $C^{16}O^{18}O$ (2338 cm⁻¹) and $C^{18}O_2$ (2331 cm⁻¹). The loss of the 2190 and 2208 cm⁻¹ is due to the surface heating (up to ~75 °C) during UV irradiation, as confirmed by a separate thermal control experiment using the same conditions as that of Figure 3, and holding the surface temperature at 75 °C for 180 min, but without photoirradiation. It is noted that after 180 min surface heating in this control experiment, carbon dioxide is also formed, but its amount is much less than that observed in Figure 3. The most important feature in Figure 3 with respect to oxygen-mixing is that the band positions of adsorbed CO, no matter which adsorption form, are not shifted under UV illumination in $^{18}O_2$, clearly indicating that no oxygen isotopic exchange occurs between $^{18}O_2$ and adsorbed CO. The IR frequencies of $C^{16}O$ and $C^{18}O$ in the gaseous state are 2143 and 2091 cm⁻¹, respectively, with 52 cm⁻¹ discrepancy. If oxygen scrambling does occur, the positions of adsorbed carbon monoxide should be shifted to lower frequencies or the bandwidth should become broader. However no detectable changes in the positions and shapes of these bands are found. In brief conclusion, the result in Figure 3 shows that $C^{16}O$ is photooxidized to $C^{16}O^{18}O$, but without oxygen exchange.

Figure 4 shows the IR spectra taken before and after the indicated times during the UV irradiation of a TiO_2 surface initially in contact with a mixture of ~0.1 Torr CO_2 and 10 Torr $^{18}O_2$. The major peaks at 1316, 1582, and 2361 cm⁻¹ in

$^{18}O_2$ Exchange of CO, CO_2, CO_3, and COOH on TiO_2

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Figure 4. IR spectra taken before and after 1, 5, 60, and 180 min during the UV exposure of a TiO_2 surface initially in a mixture of ~0.1 Torr of CO_2 and 10 Torr of $^{18}O_2$.

Figure 5. IR spectra taken before and after 5, 60, or 180 min during the UV exposure of TiO_2 covered with CO_3 initially in 10 Torr of $^{18}O_2$.

the 0-min spectrum of Figure 4, as presented in Figure 2, indicate the presence of adsorbed bidentate carbonate and carbon dioxide. After 1 min UV irradiation, the absorption intensities of these bands are reduced due to thermal desorption because of the surface heating effect upon photoillumination of TiO_2. Along with the light exposure, the surface CO_2 band originally at 2361 cm^{-1} becomes broader and the center shifts to 2347 cm^{-1} after 180 min. This change strongly suggests ^{18}O is incorporated into carbon dioxide. The broad 2347 cm^{-1} feature is due to band overlap of adsorbed $C^{18}O_2$, $C^{16}O^{18}O$, and residual $C^{16}O_2$. In terms of the 12 cm^{-1} difference between gaseous $C^{16}O_2$ (2349 cm^{-1}) and adsorbed one (2361 cm^{-1}), it is estimated that the band positions for adsorbed $C^{16}O^{18}O$ and $C^{18}O_2$ are at 2350 and 2343 cm^{-1} respectively. (Note that the absorption frequencies for gaseous $C^{16}O^{18}O$ and $C^{18}O_2$ are 2338 and 2331 cm^{-1}). We have tested the possibility of oxygen exchange between $^{18}O_2$ and CO_2 in the gas phase by using the same experimental condition as that of Figure 4 but without TiO_2. This control study shows no frequency red-shift for gaseous CO_2 and therefore this possibility is ruled out. For the change in the 1200−1800 cm^{-1} region induced by the photoillumination in Figure 4, the 1582 cm^{-1} band of bidentate carbonate is shifted to ~1570 cm^{-1} after 180 min photoirradiation, suggesting that ^{18}O is incorporated into the surface carbonate as well. However, it may not represent that the oxygen exchange is directly due to interaction of $^{18}O_2$ with adsorbed CO_3. For an example, if adsorbed $C^{16}O_2$ is scrambled with $^{18}O_2$ to form $C^{16}O^{18}O$, this species may be desorbed and readsorbed on the TiO_2 surface to form $C^{16}O^{16}O^{18}O$. To test this possibility, we have carried out an oxygen scrambling experiment for a TiO_2 surface only covered with CO_3. This surface was prepared by CO_2 adsorption on TiO_2 at 35 °C followed by evacuation at ~80 °C. As demonstrated in Figure 2, this process produces adsorbed CO_3 without the presence of CO_2. Figure 5 shows the

IR spectra taken before and after the indicated times during the UV irradiation of CO_3 on TiO_2 in 10 Torr of $^{18}O_2$. The two major bands at 1315 and 1582 cm^{-1} that belong to bidentate carbonate show different response to the UV irradiation in $^{18}O_2$. The 1582 cm^{-1} band becomes broader and is gradually red-shifted to ~1567 cm^{-1} after 180 min in contrast to the unshifted 1315 cm^{-1} band. Note that for bidentate CO_3 the 1315 cm^{-1} band is due to the stretching of $C-O_I$ in which O_I is directly bonded to the surface Ti ion; however, the 1582 cm^{-1} band is due to the stretching of $C=O_{II}$ with carbonyl character as shown in Scheme 3. The red-shift of the 1582 cm^{-1} band indicates that oxygen scrambling occurs at the $C=O_{II}$ site. The broad peak feature of 1567 cm^{-1} in the 180 min spectrum is due to band overlap of $C^{16}O_3$ and $C^{18}O_{II}^{16}O_I^{16}O_I$. It is estimated that the stretching frequency of $C=^{18}O_{II}$ for adsorbed $C^{18}O_{II}^{16}O_I$-$^{16}O_I$ is ~1552 cm^{-1}, i.e., ~30 cm^{-1} lower with respect to $C=^{16}O_{II}$ of the adsorbed $C^{16}O_3$[6] or previous reports of the change in frequency for organic molecules with carbonyl group containing ^{16}O or ^{18}O.[25] The result of Figure 5 shows that bidentate CO_3 does exchange with $^{18}O_2$ directly, not through readsorption of ^{18}O-containing carbon dioxide. Furthermore in the experiment for Figure 5, no enhanced IR absorption for carbon dioxide at ~2350 cm^{-1} was found (not shown), indicating that oxygen scrambling of carbon dioxide observed in Figure 4 is not due to transformation of ^{18}O-containing carbonate either. In addition to the peak shift of the 1582 cm^{-1} band, the 1462 cm^{-1} band seems to be slightly shifted. We tentatively do not intend to assign this shift to oxygen scrambling, because this peak is relatively small and its band position tends to be altered by the change of neighboring bands. We have also carried out a contrast experiment of UV irradiation of adsorbed carbonate in $^{16}O_2$ instead of $^{18}O_2$. No peak shift for the two bands at 1315 and 1582 cm^{-1} of bidentate CO_3 is found after 180 min.
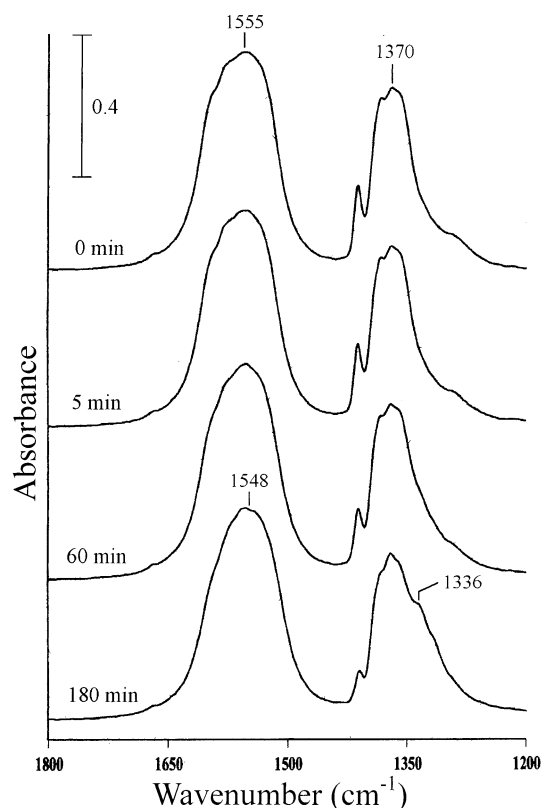
Figure 6. IR spectra taken before and after 5, 60, or 180 min during the UV exposure of TiO_2 covered with HCOO initially in 10 Torr of $^{18}O_2$.

Figure 6 shows the IR spectra taken before and after the indicated times during the UV irradiation of adsorbed HCOO on TiO_2 in 10 Torr of $^{18}O_2$. The formate-covered TiO_2 surface was prepared by exposing a clean TiO_2 surface to 2 Torr of formic acid, followed by evacuation at 210 °C for 2 min. The bands at 1370 and 1555 cm^{-1} are assigned to symmetric and antisymmetric $-COO-$ stretching of adsorbed HCOO. After 180 min light exposure, a band appears at 1336 cm^{-1} as a shoulder of the 1370 cm^{-1} band. Meanwhile, the 1555 cm^{-1} band center is also red-shifted to 1548 cm^{-1}. These strongly suggest that ^{18}O is incorporated into adsorbed formate, as supported by the consistent IR frequency shift of ^{18}O-containing formate. The frequencies of symmetric stretching of $-C^{16}O^{16}O-$ for $H^{13}C^{16}O^{16}ONa$, $-C^{16}O^{18}O-$ for $H^{13}C^{16}O^{18}ONa$, and $-C^{18}O^{18}O-$ for $H^{13}C^{18}O^{18}ONa$ are 1340, 1315, and 1297 cm^{-1} respectively,[26] and those of antisymmetric stretching of $-C^{16}O^{16}O-$ for $H^{12}C^{16}O^{16}ONa$ and $-C^{18}O^{18}O-$ for $H^{12}C^{18}O^{18}ONa$ are 1607 and 1587 cm^{-1}.[27] As one ^{16}O of $H^{13}C^{16}O^{16}ONa$ is replaced by ^{18}O, the symmetric carboxylate frequency is red-shifted by 25 cm^{-1}. This number increases to 43 cm^{-1} for $H^{13}C^{18}O^{18}ONa$. The shift in frequency for symmetric carboxylate stretching as the ^{16}O is replaced by ^{18}O is about twice of that for antisymmetric one. We have also carried out a contrast experiment of UV irradiation of adsorbed formate in $^{16}O_2$, instead of $^{18}O_2$. The peak shapes and positions for the two bands of formate at 1370 and 1555 cm^{-1} remain the same after 180 min.

Scheme 5 summarizes our findings in this research. No oxygen exchange occurs between $^{18}O_2$ and adsorbed CO; however, CO_2 and CO_3 on TiO_2 do exchange with $^{18}O_2$ under UV irradiation. Bidentate CO_3 shows bonding-dependent isotopic exchange with $^{18}O_2$. During the oxygen scrambling process in photoillumination, it is the carbonyl oxygen of bidentate carbonate, instead of the oxygen that directly bonded to the
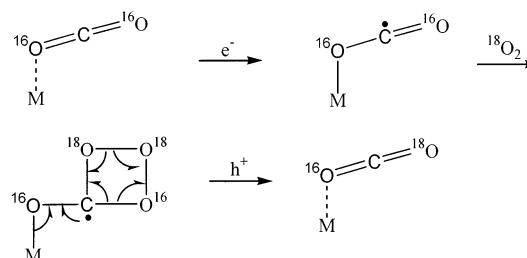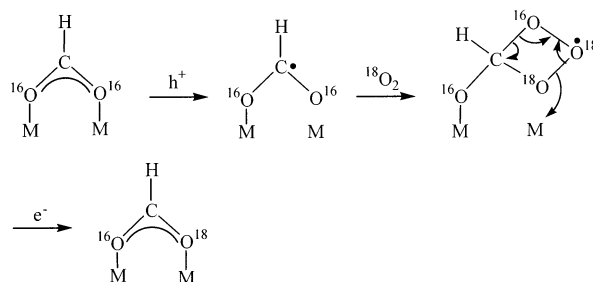
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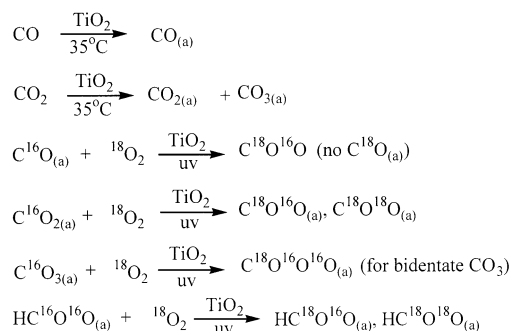
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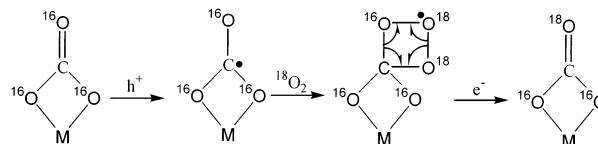
SCHEME 7

SCHEME 8

surface titanium ion, that exchanges with $^{18}O_2$. In the formate case, oxygen mixing also occurs. Schemes 6, 7, and 8 show possible mechanisms for the oxygen exchange of adsorbed carbonate, carbon dioxide, and formate with $^{18}O_2$, respectively. In the case of bidentate carbonate, the exchange process begins with hole capture followed by $^{18}O_2$ incorporation, intramolecular electron redistribution, and reception of an electron. In the case of adsorbed CO_2 with $Ti-O-C-O$ adsorption configuration, the exchange process starts with electron capture to form radicals. In the photochemical reactions of CO_2 in both homogeneous and heterogeneous systems, it is believed that CO_2 is activated by electron capture.[28,29] Therefore it is suggested that the oxygen mixing of adsorbed CO_2 with $^{18}O_2$ is initiated by photoelectron reception. After that and through the steps of $^{18}O_2$ addition, intramolecular electron redistribution, and hole reception, the oxygen exchange is completed. CO_2^- species on TiO_2 with IR bands at 1312 and 1668 cm^{-1} has been observed as CO_2 is adsorbed at -100 °C and it disappears progressively by evacuation at temperatures between -100 and 0 °C.[16] Since in our experiment for Figure 4 the surface temperature is heated to ~75 °C during TiO_2 photoirradiation and $^{18}O_2$ is present in

the reaction system, CO_2^- may not be stable and detected. In the case of adsorbed formate it has been proposed that its photodecomposition is induced by holes.[30] So the exchange is suggested to start with hole capture of adsorbed HCOO to form radical species followed by $^{18}O_2$ attachment. Through the molecular rearrangement of the O_2 adduct and electron capture, one of the oxygen atoms of adsorbed $HC^{16}O^{16}O$ is replaced by ^{18}O.

Conclusion

Scheme 5 gives a brief summary of our study of adsorption and photoassisted oxygen exchange of carbon monoxide, carbon dioxide, carbonate, and formate by in-situ FTIR. It must be pointed out that carbon dioxide, formate, or carbonate is usually the end product in photooxidation of organic molecules in the presence of oxygen. The present oxygen-exchange study may also help to elucidate reaction mechanisms in photooxidation of organics as $^{18}O_2$ is present. If an ^{18}O-containing product of carbon dioxide, carbonate, or formate is formed, it should be scrutinized whether it is due to the reaction between $^{18}O_2$ and the organics or just due to the oxygen isotopic exchange.

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