SUPPORTING INFORMATION

Oxygen-isotope labeled titania: $Ti^{18}O_2$

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S1. Sample preparation and characterization techniques

The synthesis of $Ti^{18}O_2$ was carried out in a closed all-glass vacuum apparatus. Titanium tetrachloride (99.98% Aldrich) was twice distilled in vacuum before use. 1 g of $H_2{}^{18}O$ (Cambridge Isotope Laboratories ^{18}O 97 %) was frozen in high vacuum by cooling down in liquid nitrogen bath, and the ice was contacted with 2.8 mL of $TiCl_4$ vapor through a glass-breakable valve. After both reactants had mixed completely, the cooling bath was removed and the reaction product was kept at room temperature overnight. HCl formed as a by-product was collected in a side ampoule cooled by liquid nitrogen. Subsequently, the solid product was heated at 200°C overnight in the still closed vacuum apparatus, while the HCl trap remained permanently cooled in the liquid nitrogen bath. The HCl-trap was then sealed off. (SAFETY WARNING: The cooling of HCl must not be interrupted in order to prevent hazardous overpressure in the trap. We should note that this pressure was estimated to me more than 20 bar without cooling!). Finally, the apparatus was opened in a glove box under Ar and the solid white powder was collected. This product is subsequently labeled as A200. The material was stored under Ar at room temperature. In the next synthetic step, part of the A200 powder was heated at 450°C in vacuum (10^{-5} Pa) for 30 hours. This material is labeled as A450. Eventually, this sample was calcined at 1000°C in vacuum (10^{-5} Pa) for 30 hours; this sample is labeled as R1000. Reference samples were prepared by repeating the described protocol, except for replacing $H_2{}^{18}O$ with ordinary water with natural isotope composition.

All samples were characterized by X-ray diffraction (Bruker D8 Advance diffractometer; CuKα radiation), while they exhibited the diffraction pattern of phase-pure anatase (A200, A450) or rutile (R1000). Within experimental errors, the X-ray diffractograms were identical for $Ti^{18}O_2$ and $Ti^{16}O_2$ of the same synthetic history. For instance, the lattice parameters of $Ti^{18}O_2$ (A450) were a = 3.786 Å, c = 9.511 Å and those of the light homologue $Ti^{16}O_2$ (A450) were a = 3.786 Å, c = 9.508 Å. BET from surface areas were calculated from N_2 adsorption isotherms (Micromeritics ASAP 2020 instrument).

Raman spectra were measured on a LabRam HR spectrometer (Horiba Jobin Yvon) interfaced to an Olympus BX41 microscope. The spectra were measured on powder sample either inside the hermetically sealed FTIR optical cell (see below) or simply in air. The spectra were excited by an Ar^+- laser (Innova 70C series, Coherent) using the green line, 2.41 eV (514.5 nm). The laser power impinging on the sample or the optical cell was between 1.2 to 1.6 mW. The Raman spectrometer was calibrated before each set of measurements by using the F_{1g} line of Si at 520.2 cm^{-1} as a reference.

FTIR spectra were measured in a 20-cm long (2.8 cm diameter) glass optical cell equipped with CaF_2 windows. The cell was interfaced to a sealable glass-tube joint for the transference of the powder material under vacuum from a side ampoule in which the calcination of TiO_2 also took place. (In certain experiments, this *in-situ* calcination and vacuum transfer of TiO_2 were avoided; in these cases, the optical cell was loaded with TiO_2 simply in a glove box under Ar and then evacuated.) The optical cell was further equipped with a second vacuum valve (ACE glass, USA) for the gas handling and connection to the vacuum line. For the actual isotope exchange experiment, the optical cell containing 0.8 g of $Ti^{18}O_2$ powder (A200 or A450; spread on the walls) was filled with $C^{16}O_2$ (5.3 purity, Linde Technogas). The pressure in the cell was about 2 Torr, and was precisely measured with a MKS Baratron pressure gauge (0–10 Torr). The spectral measurement was performed using the Bruker IFS 120 HR spectrometer (CaF_2 beam splitter, InSb detector) in a spectral range of 1800 - 6000 cm^{-1}. The spectra were measured with a resolution of 0.01 cm^{-1} with 30 scans using the Blackmann-Harris apodisation function. For kinetic measurements, the optical cell was left in the dark inside a thermostat at a temperature of 30±0.1 ^oC. The incurred gaseous mixture was measured after selected time by FTIR as described above.

S2. Theoretical calculations

First-principles calculations using density functional theory (DFT) with local density approximation (LDA) have been performed for both geometry optimization and vibration analysis. The Vienna *ab initio* simulation package (VASP)[1] was used with a plane-wave basis set employed within the framework of the projector augmented-wave method. The plane-wave cutoff energy was set to 500 eV. Optimization was performed until all force components fell below 3 meV/Å. A k-point set of 18 x 18 x 18 *Γ*-centered Monkhorst-Pack grid was used for geometry optimization. This means 480 and 550 irreducible points for anatase and rutile, respectively. After optimizing the geometry, calculations of the Hessian matrices (force constants) were performed using large enough supercells in order to take into account long-range force constants. The size of the supercell was 3 x 3 x 3 (162 atoms) and 3 x 3 x 5 (270 atoms) for anatase and rutile, respectively. Due to the larger supercell the k-point set was smaller: 3 x 3 x 3 (14 irreducible points) and 2 x 2 x 2 (6 irreducible points) *Γ*-centered Monkhorst-Pack grid for anatase and rutile, respectively. The displacement of the atoms was 0.01 Å. For different isotopes the dynamical matrices were obtained by different mass matrices but with the same force constants. Self made tool was employed to correct numerical inaccuracies and to ensure the appropriate symmetry of the dynamical matrix.

The involvement of different atoms in the normal modes can be characterized by the sum of the squares of all components corresponding to a given type of atom. The normal modes are normalized to unity. Table 1-S2 shows the involvement of Ti atoms for various normal modes. For sake of completeness, all modes are shown. Pure oxygen and titanium movements correspond to ratio 0 and ratio 1, respectively. In rutile, all four Raman active modes are purely oxygen movements. In anatase, there is only one mode of

this kind, viz. A_{1g}. Here the Ti atoms do not move (the ratio is 0) which can be also shown by symmetry analysis[2].

Table 1-S2. Calculated ratio of Ti movement (last column) for all normal modes of anatase and rutile. The first three columns show the calculated frequencies υ, symmetries and Raman (R) or infrared (IR) activities. Silent modes are indicated with - sign.

	υ (cm^{-1})	*Symm.*	*R / IR activity*	*Ti motion of mode*
Anatase	146.5	$E_g(1)$	R	0.9900
	154.5	$E_g(2)$	R	0.0015
	239.3	$E_u(1)$	IR	0.3364
	349.0	A_{2u}	IR	0.3856
	381.8	$B_{1g}(1)$	R	1
	452.4	$E_u(2)$	IR	0.0529
	503.7	$B_{1g}(2)$	R	0.0004
	526.9	A_{1g}	R	0
	550.3	$B_{2u}(1)$	-	0
	653.6	$E_g(3)$	R	0.0088
Rutile	93.6	$B_{1u}(1)$	-	0.9880
	138.8	A_{2u}	IR	0.3181
	141.2	B_{1g}	R	0
	142.0	$E_u(1)$	IR	0.3600
	384.7	$E_u(2)$	IR	0.5550
	400.4	$B_{1u}(2)$	-	0.0110
	419.2	A_{2g}	-	0
	466.3	E_g	R	0
	490.2	$E_u(3)$	IR	0.4225
	614.5	A_{1g}	R	0
	819.1	B_{2g}	R	0

S3. Kinetics of oxygen isotope exchange at the interface $C^{16}O_2/Ti^{18}O_2$

The concentrations of individual istopologues, *viz.* $C^{16}O_2$ (16-16), $C^{16}O^{18}O$ (16-18) and $C^{18}O_2$ (18-18) were expressed in terms of the corresponding partial pressures in the gas phase of our closed optical cell (see S1). The intensities of individual lines in HR-FTIR spectrum (cf. Fig. 3) were recalculated to partial pressures using calibration curves for each given isotopologue. Between spectral measurements, the optical cell was kept in a thermostat at 30 ± 0.1 ^{o}C (see S1).

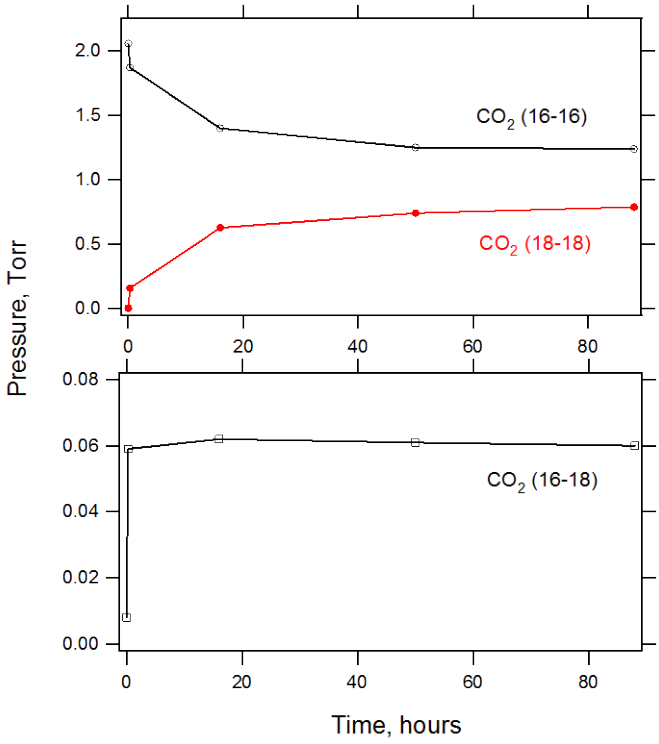

Figure 1-S3. Interaction of $Ti^{18}O_2$ (A450 sample) with carbon dioxide. Concentrations of ^{16}O-C-^{16}O, ^{18}O-C-^{16}O and ^{18}O-C-^{18}O isotopologues (Torr) as a function of time. Reaction temperature 30°C.

Reference List

1. G. Kresse and J. Furthmuller, *Phys. Rev. B* 1996, **54**, 11169-11186.
2. T. Ohsaka, F. Izumi and Y. Fujiki, *J. Raman Spec.* 1978, **7**, 321-324.