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Introduction

Selective oxidation catalysed by solid oxides is an important industrial process for converting hydrocarbons into valuable chemicals such as alcohols, aldehydes, and acids at high temperatures.^{1–3} It is known that oxidation proceeds through two independent steps that are known as the Mars–van Krevelen mechanism.⁴ In the first step surface oxygen atoms are incorporated into the substrate, yielding oxygenated products and simultaneously producing oxygen vacancies on the oxide surface. In the second step, the vacant sites are filled by molecular oxygen.⁵ Accordingly, the gas-phase oxidation occurs at the surface of the solid oxide. The Mars–van Krevelen mechanism has been widely used to explain heterogeneous catalytic reactions that typically occurs at high temperature.^{4,6–8}

It has been reported that the Mars-van Krevelen mechanism can be applied to homogeneous catalytic reactions performed in solution under mild conditions, specifically oxidation promoted by soluble polyoxometallate compounds under an oxygen atmosphere.^{9,10} It has also been claimed that photocatalytic oxidation of hydrocarbons over titanium diox-

Evidence for light-induced oxygen exchange in the oxidation of liquid hydrocarbons on oxygen 18-labelled titanium dioxide[†]

Jongmyung Choi,^a Donghyeon Kang,^a Kyu Hyung Lee,^a Byeongno Lee,^a Kyung Joong Kim^b and Nam Hwi Hur*^a

Titanium dioxide (TiO₂) nanoparticles labelled with ¹⁸O isotopes were prepared *via* a sol–gel method with titanium alkoxide and ¹⁸O water precursors. The presence of ¹⁸O in the labelled TiO₂ sample was confirmed using Raman spectroscopy and secondary-ion mass spectrometry. The photocatalysis of cyclohexane under UV light was investigated using ¹⁸O-labelled TiO₂ as the catalyst; this reaction yielded ¹⁸O-containing cyclohexanone as the major product. The ¹⁸O content in the cyclohexanone product dramatically decreased with increasing reaction time. This isotopic experiment demonstrates that the oxygen atom in cyclohexanone originates from surface oxygen in ¹⁸O-labelled TiO₂. Similar photoreactions performed with toluene and *para*-xylene as the hydrocarbon substrates afforded oxidation products containing ¹⁸O isotopes. The migration of oxygen atoms in ¹⁸O-labelled TiO₂ into liquid hydrocarbons provides direct evidence for the involvement of the solid oxide in the interfacial reaction between a liquid substrate and surface oxygen in a solid catalyst.

ide (TiO₂) can be explained via the Mars-van Krevelen mechanism. Almeida and co-workers investigated the photooxidation of cyclohexane over anatase TiO₂ under an ¹⁸Olabelled oxygen (O2) atmosphere using attenuated totalreflectance Fourier-transform infrared (FT-IR) spectroscopy; their results suggest that the oxygen in the cyclohexanone product originates as surface oxygen in TiO2.8 Civiš and coworkers reported that surface oxygen in TiO₂ and oxygen in CO₂ can be exchanged during photo-reactions;¹¹ they studied light-induced oxygen exchange between ¹⁸O-labelled TiO₂ and CO₂ molecules using a high-resolution IR spectrometer. Although their labelling studies did not include any mass spectral data, it is conceivable that the surface oxygen in TiO₂ plays a crucial role in the photo-oxidation of gaseous hydrocarbon molecules. Light-induced gas-to-solid reactions over TiO2 surfaces are quite analogous to the oxidation of hydrocarbons catalysed by solid oxides at high temperature. We thus reasoned that, under ambient conditions, the same photo-oxidation process might occur at the liquid-solid interface, and oxygen transfer from TiO2 to the liquid substrate would provide direct evidence of the Mars-van Krevelen mechanism.

Herein we demonstrate that the photo-oxidation of cyclohexane over ¹⁸O-labelled TiO₂ under UV irradiation afforded ¹⁸O-labelled cyclohexanone as the major product. The ¹⁸Oisotope labelling experiments along with the mass spectrometric product analyses clearly demonstrate that oxygen atoms in the TiO₂ surface are transferred to the oxidation products.

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^aDepartment of Chemistry, Sogang University, Seoul 121-742, Korea. E-mail: nhhur@sogang.ac.kr

^bDivision of Industrial Metrology, Korea Research Institute of Standards and Science, Daejeon 305-600, Korea

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To further confirm this result, the same photocatalytic experiments were performed using toluene and *para*-xylene as the hydrocarbon substrates; the corresponding ¹⁸O-labelled products were obtained, thereby confirming that the oxygen atoms in the oxidation products originate from the surface oxygen atoms in ¹⁸O-labelled TiO₂. Our results provide direct evidence that photocatalytic reactions that occur at liquid-solid interfaces can also be explained by the Mars-van Krevelen mechanism.

Experimental

Synthesis and characterization of ¹⁸O-labelled TiO₂

¹⁸O-labelled TiO₂ was prepared in a stainless steel autoclave (Parr 4714, 45 mL) according to the following procedure: the glass liner of the autoclave was charged with 4 mL of tetraisopropyl orthotitanate (TCI) and 1 mL of H₂¹⁸O (Cambridge Isotope Laboratories, 97%). After the gauge and gauge-block assembly were attached to the autoclave, the autoclave was placed in an oil bath on a hot plate. After heating at 200 °C for 3 h, the autoclave was removed from the oil bath. The white crystalline solid that formed on the bottom of the glass liner was filtered and washed with ethanol several times to remove the isopropyl alcohol and water. The solid product was then completely dried in an oven at 80 °C. The yield of ¹⁸O-labelled TiO₂ based on the amount of tetraisopropyl orthotitanate used was typically greater than 92%. The ¹⁸Olabelled TiO₂ powder was characterized using powder X-ray diffraction (XRD), transmission electron microscopy (TEM), Raman spectroscopy, and secondary-ion mass spectrometry (SIMS) depth profiling. The powder XRD patterns were obtained using a Rigaku diffractometer (Cu-Ka) operating at 40 kV and 150 mA. TEM analyses were carried out on a JEOL JEM-2100F. Raman spectra were obtained at room temperature using a LabRam HR Raman spectrometer (Horiba Jobin-Yvon) equipped with a liquid-nitrogen-cooled CCD multichannel detector. A 514 nm Ar-ion laser was used as the excitation source. The relative ratio of ¹⁶O and ¹⁸O in the ¹⁸O-labelled TiO₂ was determined using SIMS depth profiling with a magnetic sector SIMS (IMS-7f, Cameca). A cesium-ion beam was used as the primary ion source to enhance the negative ion intensity. For comparison, unlabelled TiO₂ was prepared following the same procedure with deionized water (H₂O) in place of H₂¹⁸O; the product was then characterized in a similar manner.

Photocatalytic reaction

A 0.16 g sample of ¹⁸O-labelled TiO_2 was placed in a 2 mL vial that was sealed with a screw cap and then dried at 150 °C for 4 h *in vacuo* to remove adsorbed water. Cyclohexane (99.5%, Aldrich) was dried using molecular sieves (Aldrich) and then degassed three times *via* the freeze-pump-thaw method to afford anhydrous cyclohexane. A 0.8 mL aliquot of anhydrous cyclohexane was added to the sealed vial using a syringe. Oxygen gas (99.995%, Aldrich) was then flowed into the vial to saturate the atmosphere with O₂. The ¹⁸O-labelled TiO₂ powder dispersed in cyclohexane was irradiated with UV light

 $(\lambda > 300 \text{ nm})$ using a 300 W xenon Lamp (Newport). The incoming light was passed through a water filter to block infrared radiation. The measurements were conducted over 12 h. The products that evolved from the liquid substrate were initially analysed using a gas chromatograph (GC; Younglin, Acme-6000) equipped with a flame ionization detector. To enable quantitative analysis, the peak areas were calibrated with authentic samples. In addition to the GC measurements, the ¹H NMR spectra were also recorded on a Varian 400-MHz Gemini operating at 400 MHz. All chemical shifts were referenced to CDCl₃ at 7.26 ppm.

The ¹⁸O contents of the products were quantitatively determined from mass spectra that were obtained using a GC combined with a mass spectrometer (Agilent 5973N) at the Organic Chemistry Research Centre in Sogang University. Similar experiments were performed with toluene (99.5%, Aldrich) and *para*-xylene (>99%, Aldrich) in place of cyclohexane.

Results and discussion

The ¹⁸O-labelled TiO₂ sample prepared from tetraisopropyl orthotitanate and H_2 ¹⁸O in an autoclave was first characterized using powder XRD. Fig. 1 shows an XRD pattern of the ¹⁸O-labelled TiO₂. All peaks are well-indexed to theoretical diffraction peaks of anatase TiO₂ and no peaks corresponding to rutile TiO₂ phase were evident. The diffraction peaks are broad as a result of the nanometre-scale sizes of the particles.¹² The average crystallite size, which was calculated using the Scherrer equation, is 7.1 nm. Fig. 2 shows a high-resolution TEM image of the ¹⁸O-labelled TiO₂ sample. It appears that particles are evenly dispersed without severe agglomeration. Their average size, estimated from the TEM image, is approximately 6–9 nm, which agrees well with the XRD result.

Raman spectroscopy was employed to verify the presence of ¹⁸O in the ¹⁸O-labelled TiO₂ sample; the ¹⁸O isotope induces significant shifts and splitting of active Raman vibrational modes. It is known that anatase TiO₂ has six Raman-active vibrations including one A_{1g} , two B_{1g} , and three E_{g} modes. ^{13,14}



Fig. 1 XRD pattern of ¹⁸O-labelled TiO₂. All the XRD peaks are indexed on the basis of theoretical patterns of anatase TiO_2 .



Fig. 2 Typical TEM image of as-synthesized ¹⁸O-labelled TiO₂ particles.

Only the A_{1g} mode is ascribed to purely oxygen vibrations while the B_{1g} mode is associated with titanium vibrations. The other four vibrational modes are attributed to combined oxygen and titanium vibrations.¹⁵ As shown in Fig. 3, the A_{1g} mode at 513 cm⁻¹ in the Raman spectrum of ¹⁸O-labelled TiO₂ was red-shifted relative to that in the spectrum of unlabelled TiO₂, but the $B_{1g(1)}$ peak was virtually unchanged at 399 cm⁻¹. An isotopic shift was also observed in the $E_{g(3)}$ mode at 639 cm⁻¹. However, the other three modes were not discernible in the Raman spectrum because the $B_{1g(2)}$ peak overlaps with the A_{1g} mode and the two other E_{g} modes appear far below 160 cm⁻¹. The distinctive shift of the Raman peaks in the ¹⁸Olabelled TiO₂ sample provides direct evidence for the ¹⁸O labelling of TiO₂.

To determine the relative ¹⁸O and ¹⁶O contents of the ¹⁸Olabelled TiO₂ sample, compositional SIMS depth profiling was employed with a caesium-ion beam as the primary ion source to enhance the negative ion intensity.¹⁶ The relative ratio of ¹⁶O and ¹⁸O isotopes is directly determined from the intensities of ¹⁶O and ¹⁸O since their ionization yields remain nearly constant due to their same chemical properties. As shown in Fig. 4, ¹⁶O and ¹⁸O are evenly distributed in the ¹⁸Olabelled TiO₂ sample: the relative percentages of ¹⁶O and ¹⁸O



Fig. 3 Raman spectra of $^{18}\text{O}\text{-labelled}\ \text{TiO}_2$ (red curve) and unlabelled TiO_2 (dashed curve) excited by a 514.5 nm laser. The inset is an enlarged view of the same Raman spectra.



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Fig. 4 SIMS depth profile of ¹⁸O-labelled TiO₂ as a function of time. The red, blue, and black curves correspond to the signals from ¹⁸O, ¹⁶O, and ⁴⁸Ti, respectively. The inset is the relative percentages of ¹⁶O and ¹⁸O.

in the labelled sample are 38.56% and 61.44%, respectively. It is worth mentioning that a $Ti^{18}O_2$ sample that contains mainly ¹⁸O isotopes has been prepared from $TiCl_4$ and H_2 ¹⁸O;¹⁴ however, this process results in chlorine-contaminated product. Our method, which is based on titanium alkoxide, avoids chlorine contamination to afford the chlorine-free ¹⁸O-labelled TiO_2 product, albeit with an isotopic mixture of ¹⁸O and ¹⁶O.¹⁷ However, this product is better suited to studying the oxidation of various organic substrates over titanium oxide because of the absence of chlorine impurities.

On the basis of these initial characterization results, we investigated the photo-oxidation of cyclohexane with ¹⁸O-labelled TiO₂ to elucidate the involvement of the surface of the titanium oxide in the oxidation process. The photocatalytic reaction was performed under UV irradiation in an O₂ atmosphere, yielding cyclohexanone as the major product along with a small amount of cyclohexanol. Over 90% selectivity towards cyclohexanone was achieved, which is similar to that obtained in previous studies.^{18–20} High selectivity towards cyclohexanone was also confirmed by the ¹H NMR spectra, which are shown in Fig. S1, ESI.[†] We carefully monitored the reaction over time by analysing the ¹⁸O/¹⁶O ratio *via* mass spectrometry and gas chromatography. A control experiment was also performed using unlabelled TiO₂ as the photocatalyst.

The top and bottom panels of Fig. 5(a) show two mass spectra of cyclohexanone obtained from reactions over ¹⁸Olabelled and unlabelled TiO₂ catalysts, respectively. The mass spectra of both cyclohexanones show molecular ion (M+) peaks at m/z = 98. In addition, a small peak appears at M+1 in each spectrum, which represents small amounts of isotopically substituted cyclohexanones containing natural ¹³C and ²H isotopes.²¹ However, the spectra differ significantly in their isotopic peaks because of the ¹⁸O isotopes in the cyclohexanone generated over ¹⁸O-labelled and unlabelled TiO₂. A distinctive M+2 peak at m/z = 100 is evident only in the cyclohexanone generated from the ¹⁸O-labelled TiO₂ catalyst, which clearly indicates that ¹⁸O isotopes are present in the product. This ¹⁸O isotope experiment provides direct evidence



Fig. 5 Selected mass spectral data of (a) cyclohexanone, (b) benzaldehyde, and (c) 4-methylbenzaldehyde produced on ¹⁸O-labelled TiO₂ (red line) and unlabelled TiO₂ (black line). The asterisks mark the molecular ion peaks that contain ¹⁸O.

for the incorporation of oxygen atoms from ${\rm TiO}_2$ into cyclohexane.

To confirm the migration of surface oxygen from TiO_2 into the product, the scope of the photo-reactions was expanded to include toluene and *para*-xylene as hydrocarbon substrates.^{2,22} The oxidation of toluene and *para*-xylene yielded mainly benzaldehyde and 4-methylbenzaldehyde, respectively, which were evidenced by ¹H NMR spectra (Fig. S2 and S3, ESI†). Other products such as benzoic acid and 4-methylbenzoic acid were not observed in the ¹H NMR spectra. Their signals usually appear at about 12.5–13.0 ppm. Accordingly, we could exclude the possibility of formation of carboxylic acid derivatives from the UV irradiation of toluene and *para*-xylene with TiO₂.

As anticipated, a distinctive M+2 peak at m/z = 108 was observed in the mass spectrum of benzaldehyde obtained from the photo-oxidation of toluene over ¹⁸O-labelled TiO₂ (top panel of Fig. 5(b)). Fig. 5(c) shows the mass spectra of 4-methylbenzaldehyde generated from the photo-oxidation of *para*-xylene over unlabelled (bottom panel) and ¹⁸O-labelled (top panel) TiO₂ catalysts. As anticipated, the presence of an additional peak at m/z = 122 that corresponds to the M+2 peak provides clear evidence of the participation of oxygen from the TiO₂ surface in the oxidation process. The additional ¹⁸Olabelled experiments confirmed the migration of surface oxygen into the oxidation products; this result suggests that the Mars–van Krevelen mechanism is also valid for photocatalytic reactions at liquid–solid interfaces.

To elucidate the role of the surface TiO_2 oxygen in hydrocarbon oxidation and the mechanism by which the oxygen vacancies in TiO_2 are filled, we carefully determined the ¹⁸O content of the cyclohexanone product as a function of



Fig. 6 Cyclohexanone formation *via* the photocatalytic oxidation of cyclohexane over ¹⁸O-labelled TiO₂ as a function of time. The left vertical axis represents the concentration of cyclohexanone(\blacksquare) and the right axis is the percentage of ¹⁸O isotope included in cyclohexanone(\blacktriangledown). The horizontal axis is the UV-irradiation time.

irradiation time, which is shown in Fig. 6. With increasing irradiation time, the amount of cyclohexanone produced from the reaction over ¹⁸O-labelled TiO₂ increases almost linearly while the ¹⁸O content of the cyclohexanone drastically decreases. These time-dependent ¹⁸O data suggest that only surface oxygen in TiO₂ interacts with cyclohexane over the entire reaction period and bulk oxygen does not participate in the oxidation reaction. In detail, cyclohexane initially reacts with surface oxygen atoms to form cyclohexanone, leaving behind oxygen vacancies on the TiO₂ surface.²³ Subsequently, the oxygen vacancies that are associated with reduced titanium cations, presumably Ti³⁺, are filled by ¹⁶O atoms from atmospheric O_2 .^{24–26} As the reaction proceeds, a large number of ¹⁶O atoms are integrated into the TiO₂ surface, producing a ¹⁶O-rich TiO₂ surface and eventually resulting in the production of ¹⁶O-rich cyclohexanone. Labelling experiments also indicate that exchange between the ¹⁸O atoms in TiO₂ and the ¹⁶O atoms in molecular oxygen (O_2) is less likely to occur.^{27–30} It is also important to note that the bulk oxygen atoms in TiO_2 did not readily diffuse into the oxygen vacancies on the TiO₂ surface.31-33 To show that bulk oxygen atoms did not diffuse into the vacant sites in surface, we carefully examined the Raman spectra of fresh and used ¹⁸O-labelled TiO₂ samples. As shown in Fig. S4, ESI,[†] both Raman spectra are virtually identical. This indicates that the ¹⁸O and ¹⁶O atoms are not exchanged within the TiO₂ lattice. It is thus conceivable that oxygen vacancies are filled solely by O2 at the liquid-solid interface. It has been shown that O₂ molecules diffuse freely across the oxide surface and dissociate to fill oxygen vacancies on oxide surfaces.25,26,34-36

Based on the observed isotopic distribution of the ¹⁸O atoms in cyclohexanone, we envision that the oxidation of cyclohexane and subsequent filling of oxygen vacancies in the TiO₂ surface may occur *via* the following steps, which are schematically illustrated in Fig. 7: the first step is the formation of cyclohexanone by the interaction of cyclohexane with surface TiO₂ oxygen (¹⁸O/¹⁶O). In the subsequent step, the



Fig. 7 A schematic diagram of the reaction mechanism of the formation of cyclohexanone on $^{18}\mbox{O-labelled TiO}_2.$

resultant oxygen vacancy on the TiO₂ surface is filled by $({}^{16}O)_2$ that is dissolved in the cyclohexane; the $({}^{16}O)_2$ molecule adsorbs on the TiO₂ surface, dissociates, and fills two vacant sites presumably *via* diffusion of an oxygen atom produced from the dissociated $({}^{16}O)_2$ molecule to a neighbouring vacant site. Continuous reactions of cyclohexane on the TiO₂ surface eventually yield ${}^{16}O$ -rich cyclohexanone.

Conclusions

In summary, we successfully prepared chlorine-free, anatasephase ¹⁸O-labelled TiO₂ in an autoclave. By using the ¹⁸Olabelled TiO₂ as a photocatalyst, we demonstrated that the oxygen atoms in the products generated from the photocatalytic oxidation of hydrocarbons originate from surface oxygen in TiO₂. It was also determined that O₂ molecules dissolved in the hydrocarbon substrate fill the oxygen vacancies in TiO₂. Our isotopic labelling results clearly demonstrate that the Mars-van Krevelen mechanism accounts for the photo-oxidation that occurs at the liquid-solid interface.

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