

# Letter

# In Situ Observation of Stepwise C–H Bond Scission: Deciphering the Catalytic Selectivity of Ethylbenzene-to-Styrene Conversion on TiO<sub>2</sub>

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**ABSTRACT:** The conversion of light alkanes to olefins is crucial to the chemical industry. The quest for improved catalytic performance for this conversion is motivated by current drawbacks including: expensive noble metal catalysts, poor conversion, low selectivity, and fast decay of efficiency. The in situ visualization of complex catalysis at the atomic level is therefore a major advance in the rational framework upon building the future catalysts. Herein, the catalytic C–H bond activations of ethylbenzene on TiO<sub>2</sub>(110)-(1 × 1) were explored with high-resolution scanning tunneling microscopy and first-principles calculations. We report that the first C–H bond scission is a two-step process that can be triggered by either heat or ultraviolet light at 80 K, with near 100% selectivity of  $\beta$ -CH bond cleavage. This work provides fundamental understanding of C–H bonds cleavage of ethylbenzene on metal oxides, and it may promote the design of new catalysts for selective styrene production under mild conditions.



The selective dehydrogenation of saturated hydrocarbons ↓ via sp<sup>3</sup> C−H bond activation is an attractive approach to selectively produce fine chemicals, such as alkenes and styrene, due to the notion of step economy and environmental friendliness. However, on account of the inertness of the sp<sup>3</sup> C-H bonds, most industrial selective dehydrogenation processes require a harsh environment, involving elevated temperatures and high pressures, for example, on-purpose dehydrogenation of light alkanes.<sup>1,2</sup> Recently, neoteric catalysts have been proposed for such direct C-H bond activations along with the emerging of new catalytic active sites.<sup>3–8</sup> For example, coordinatively unsaturated metal cations and structurally confined metal atoms have been reported as desired active sties for higher efficiency and selectivity.9-12 In comparison with other characterization technologies, highresolution scanning probing microscopies (SPM) can provide atomic-scale and real-space information on not only the active sties (e.g., the local density of states and the coordination numbers) but also the reaction species (e.g., chemical identities, electronic characteristics, and binding configura-tions).<sup>13–23</sup> Correspondingly, SPMs have been extensively employed in the studies of the reaction mechanisms of the onsurface dehydrogenation reactions.<sup>24,25</sup> For instance, Chi et al. reported the thermal excited C-H bond activations of the long-chain normal alkanes on a reconstructed Au (110) surface.<sup>26</sup> However, such atomic-scale studies have been

limited to the thermal excited C-H bond cleavage and subsequent C-C bond formations of alkanes on simple catalysts, such as surfaces of single crystals. The investigations toward industrial relevant dehydrogenations of hydrocarbons catalyzed by abundant and cheap metal oxides, however, are rarely reported.

Styrene is an important starting material in the synthesis of polymers such as polystyrene, styrene-acrylonitrile, and acrylonitrile-butadiene styrene.<sup>27</sup> Industrially, styrene is typically produced by the oxidative dehydrogenation of ethylbenzene (EB) using potassium-promoted iron oxide catalysts at 823–923 K in the presence of a large amount of superheated steam as heat carrier.<sup>27–29</sup> In the present work, high-resolution scanning tunneling microscopy (STM) is employed to explore the catalytic performance of the rutile  $TiO_2(110)$  surface in EB dehydrogenations, with fine control of the intermediate states of the reaction process. To observe in situ stepwise catalysis with atomic resolution, a model reaction system is designed: (1) The activation energies of

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**Figure 1.** High-resolution STM visualizing the intermediate states of the reaction. In situ STM images of the bare (a), after EB molecules adsorption (b), and followed by 355 nm laser irradiation (10 mW, 8 min) (c) on the rutile  $TiO_2(110)-(1 \times 1)$  surface at 80 K. The dashed circles in (a, b) indicate the adsorption sites of EB molecules. The dashed rectangle in (a, c) inform that the added H atom was observed after the UV light irradiation. The blue and green arrows in (b, c) indicate that two new species (I and II) appeared after the UV light irradiation. (d–f) Enlarged topographic STM images of adsorbed EB molecules, species I and II, respectively. The corresponding line profiles along the dashed lines are shown below. The "X" label in (d) marks the  $O_v$  site before EB adsorption. Image size:  $15 \times 15 \text{ nm}^2$  for (a–c),  $1.5 \times 1.5 \text{ nm}^2$  for (d–f). (b, d) Acquired at +1.20 V, 10 pA. All the other images were acquired at +1.20 V, 100 pA.

dehydrogenations are investigated by the introduction of ultraviolet light or direct electron injection from the STM tip so that the elementary reactions can be triggered step-by-step in ultrahigh vacuum (UHV); (2) only small amounts of EB molecules are deposited on the rutile  $\text{TiO}_2(110)$ - $(1 \times 1)$  surface. With systematic studies, we show that the photocatalytic C–H bond scission in EB occurs at only 80 K, with a near 100% selectivity for  $\beta$ -CH bond cleavage. The rate-determining step of styrene production is the subsequent  $\alpha$ -CH bond breaking. The catalytic selectivity is originated from the stable configuration of coadsorbed phenylethyl radical and dissociated H on the lattice O atom of TiO<sub>2</sub>.

We performed the thermal catalytic experiments of ethylbenzene dehydrogenation on  $TiO_2$  (P25) and found that the EB can be converted into styrene with an ultrahigh selectivity (>95%) at the mild condition of ~420 K (Figure S1 in the Supporting Information). Despite outstanding catalytic selectivity, the reaction mechanism remains ambiguous. Exploring in-depth mechanisms of such heterogeneous catalysis using STM is a well-known challenge, because realistic catalysts often possess a mixture of phases with various sites on different crystal facets. However, the ultrahigh yield of styrene (>95%) in this experiment strongly implies that the EB dehydrogenation taking place at all kinds surfaces of P25 is selective. This may further suggest that the reaction path on different surfaces of TiO<sub>2</sub> is similar. On the basis of this assumption, the rutile  $TiO_2(110)$ - $(1 \times 1)$ , an abundant surface in P25, is selected to study the reaction mechanism with high-resolution STM.

A typical STM image at a positive bias voltage (Figure 1a) shows a clean and well-ordered rutile  $TiO_2(110)-(1 \times 1)$ surface with bridge-bonded oxygen (BBO) vacancies. After the deposition of ~0.01 monolayer (ML) EB on the  $TiO_2(110)$ surface held at 80 K, the EB molecules yield fuzzy "cashewshaped" protrusions with the following adsorption characterizations (Figure 1b). First, these protrusions locate exclusively on the Ti rows with a tail on top of the adjacent oxygen vacancy (marked within yellow dashed circles). Second, these protrusions can be pushed from one side of the oxygen vacancy to the other side by gentle tip manipulation (Figure S2 in the Supporting Information), and they show considerable mobility on the surface (Figure S3 in the Supporting Information). These protrusions are assigned as physisorbed EB molecules with their intact configurations under given conditions. The fuzziness shown in the high-resolution image of single EB molecules (Figure 1d) suggests that the acquired image may represent a time average of the EB molecule moving with tip scanning. It has been reported that, on the rutile-TiO<sub>2</sub>(110) surface, benzene molecules lie parallel on top of Ti rows.<sup>30</sup> Thus, the EB molecules here should weakly adsorb on  $TiO_2(110)$  with phenyl rings trapped by oxygen vacancies, while alkyl tails remain mobile.



**Figure 2.** Evolution of the photochemical process of the adsorbed EB molecules on  $TiO_2(110)$  under multiple irradiation periods at 80 K. (a–f) Image size of 15 × 15 nm<sup>2</sup>, acquired at bias of +1.25 V and set point current of 100 pA, except the set point of (b) is 10 pA. UV light: 355 nm, 10 mW.



Figure 3. Statistical results of EB molecules, I, II, and H by tracing six areas of  $15 \times 15$  nm<sup>2</sup> during in situ photocatalysis (refer to the Supporting Information for detailed information).

All the fuzzy protrusions disappear when the surface was irradiated with UV light (10 mW, 355 nm) for 8 min (Figure 1c). New species I and II, indicated by blue and green arrows, are observed. During in situ continuous scanning, we found that species I exhibited a similar mobility as EB molecules.

Species II, however, is stable even when manipulated with the tip. Accompanied with the emergence of species I and II, the third surface species imaged as a dim spot (marked within the dashed box in Figure 1c) is seen. According to previous STM observations, the third surface species are assigned to the

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Figure 4. The reaction pathway of EB dehydrogenation on  $TiO_2$ . The calculated configurations, relative energies, and simulated STM images of the EB molecule, structure I, structure II, and styrene molecule on a  $TiO_2(110)$  surface, respectively.

bridging hydroxyls  $(OH_{BBO})$  on TiO<sub>2</sub>(110).<sup>31–33</sup> Taking into account that these OH<sub>BBO</sub> do not exist prior to the UV irradiation, H atoms of OH<sub>BBO</sub> should come from EB molecules, thus providing direct evidence that the C–H bonds of the adsorbed EB molecules are dissociated under the UV irradiation.<sup>33</sup>

Consecutive photocatalysis experiments with different UV light irradiation periods are performed subsequently to understand the evolution of EB molecules to structure I and II (Figure 2). Considering that EB molecules and species I are quite mobile on  $TiO_2(110)$ , instead of tracking each single adsorbate, an area of  $15 \times 15 \text{ nm}^2$  and a total of 10 areas are monitored. After 2 min of UV light irradiation (10 mW), most EB molecules change into species I, accompanied by the appearance of a small amount of II and H atoms (Figure 2c and Figure S4) (2 min), possibly due to an uneven photoreaction rate. The surface was then exposed to UV irradiation for 3, 11, and 20 min.

Figure 3 shows the change in numbers of structures I, II, and H with UV irradiation periods (Figure S4, Table S1). The reduction of structure I is very close to the increment of structure II and H atoms. The slight increase of molecules may be caused by the photoinduced deposition of EB molecules, which are previously adsorbed on the tip or sample holder nearby. On the basis of the statistical results of the irradiation experiments, it can be concluded that EB molecules experienced two consecutive photochemical processes shown in eq 1:  $EB \rightarrow I$  and  $I \rightarrow II+H$ , and the dehydrogenation is highly monoselective. Figure 3 show that these two reactions proceed without any induction period. The photoreaction from EB to species I is almost instant. Because of the approximate exponential increase of species II, the reaction from I to II is considered as a first-order reaction. STM experiments show that structure II adsorbs tightly on  $TiO_2(110)$  and rarely changes under further UV light irradiations, suggesting it is a stable product under experimental conditions. The reversed individual processes, such as  $II \rightarrow I$  and  $I \rightarrow EB$ , were not observed in the present experiment, indicating that the aforementioned reactions of EB on  $TiO_2(110)$  are irreversible at low temperatures.

With density functional theory (DFT) calculations and STM simulations, we then turn to reveal the chemical identities of structures I and II and to rationalize reaction pathways. The

binding configurations of EB on  $TiO_2(110)$  are studied first. As shown in Figure S5, different adsorption structures of EB molecules have similar energies, indicating that EB should bond weakly to the  $TiO_2$  surface via van der Waals interactions. In the most stable configuration, the phenyl group of EB sits between two adjacent Ti rows, with the backbone of the ethyl group nearly parallel with the Ti rows. The simulated STM image of such a structure is consistent with experimental observations (see Figure 1b and Figure 4). Taking also into consideration the high mobility of structures shown in Figure 1b and the reservation of chemical composition from EB, it can be concluded that the featured protrusions in Figure 1b should be adsorbed EB molecules.

Subsequently, the C-H bond scission of EB is investigated. As shown in Figure S6, in a vacuum, the reaction energies of C-H bond breaking with respect to the energies of gas-phase H<sub>2</sub> and EB are 6.38, 5.03, and 6.00 eV on the  $C(sp^2)_{arom}$ ,  $\alpha$ -C(sp<sup>3</sup>), and  $\beta$ -C(sp<sup>3</sup>), respectively. The stability of an  $\alpha$ carbon radical can be interpreted by the electron-donating effect of methyl and phenyl groups. On the  $TiO_2(110)$  surface, as Ti atoms are terminated by oxygen, the catalytic sites are regarded as exposed oxygen atoms. As seen in Figure S7, when the dissociated H and the resulting C<sub>8</sub>H<sub>9</sub> radical are coadsorbed on an O atom, the reaction energies are 0.90, 0.65, and -0.10 eV, when the C-H bond scission occurs on  $C(sp^2)_{arom}$ ,  $\alpha$ - $C(sp^3)$ , and  $\beta$ - $C(sp^3)$ , respectively. The  $\beta$ -carbon radical exhibits the highest stability. The  $\alpha$ -carbon radical is less stable due to the stereo hindering between the phenyl ring and the TiO<sub>2</sub> surface. As seen in Figure 4, the simulated STM image of the configuration shown in Figure S7c agrees well with the STM observations of structure I, in which the protrusion occupies three Ti5c sites on the Ti5c row and expands to the adjacent Ob ridge. Taking into account that the reaction energies of such kind of C-H bond cleavage is only -0.10 eV, it should be reversible. This fits with the experimentally observed mobility of structure I. Therefore, the chemical identity of structure I can be ascribed to the coadsorbed phenyl-ethyl radical and dissociated H on the same oxygen atoms. Considering that structures I and II appear at the same time under UV light irradiation and that the conversion of I to II releases an H atom, we expect that structure II is produced by the diffusion of the dissociated H atom in structure I. As shown in Figure S8, the dissociated H

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# ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.0c02729.

General method of STM, selective thermal catalytic conversion of ethylbenzene to styrene, STM images, in situ UV irradiation experiment, results (data) of adsorption and photoreaction of ethylbenzene and pdiethylbenzene, theoretical calculations, dehydrogenation of p-diethylbenzene (PDF)

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atom in I may diffuse onto a neighboring O atom with an energy drop of 0.63 eV. This process is irreversible due to the energy uphill. Combining the above analysis and the STM simulation (Figure 4), structure II is assigned to the phenylethyl radical bonded with a surface oxygen atom. Starting from this configuration, Figure S9 shows that the dissociation of a second H atom for producing the styrene molecule involves an energetic cost of 1.20 eV. Correspondingly, the second C-H bond scission is expected to be the rate-limiting step. The full energy diagram of EB dehydrogenations based on our calculations is depicted in Figure 4; the catalytic selectivity resulted from the first C-H bond cleavage, in which the reaction energy of the H dissociation from the  $\beta$ -C(sp<sup>3</sup>) atom is at least 0.75 eV lower than those from the  $\alpha$ -C(sp<sup>3</sup>) atom and the C(sp<sup>2</sup>) atom. The produced  $\alpha$ -C(sp<sup>3</sup>) radicals are stabilized when the dissociated H atoms diffuse away. The cleavage of the second C-H bond needs to overcome a large energy barrier and should be the rate-determining step in the generation of styrene.

In addition to photocatalysis, we show that in situ productions of I to II can also be achieved by the injection of tunneling electrons as shown in Figure S10, which has been developed as a routine method to identify chemical changes on a surface.<sup>34</sup> The STM tip was positioned over the center of a single I indicated with the "star" in Figure S10a, and a voltage pulse (2.5 V at 1.0 nA for 10 ms) was then applied with the feedback loop turned off. A rescan of the same area after electron injection (Figure S10b) shows that structure I adsorbed parallel to the [001] direction has transformed to the perpendicular direction, with the formation of a small dim spot on the oxygen bridge nearby. After another voltage pulse performed at the "star" place as indicated in Figure S10b, the dim spot disappeared (Figure S10c), which is consistent with the behavior of H  $(OH_{BBO})$ . These results demonstrate that the  $\beta$ -CH bond of EB can also be broken by inelastic electron tunneling, which implies that, under UV light irradiation, the photocleavage of a C-H bond may proceed via the interaction with photogenerated carriers.

In addition to EB, the photocleavage of the  $\beta$ -CH bond of an aromatic alkane is further confirmed by the photodissociation of *p*-diethylbenzene on the TiO<sub>2</sub>(110) surface (Figure S11, in the Supporting Information). Upon UV-light illumination, *p*-diethylbenzene will lose one H atom on a  $\beta$ -C atom and form a similar chemically bonded moiety. Hence, such an approach of facile and highly selective photocatalytic C-H bond dissociation of aromatic alkane on the TiO<sub>2</sub> surface is general and can be adopted for more applications.

In conclusion, combining high-resolution STM measurements, photocatalysis, and first-principles calculations, we demonstrated that the selective dehydrogenation of EB molecules can be catalyzed by TiO<sub>2</sub> at mild conditions of ~400 K. The dehydrogenation is initiated by the selective dissociation of a hydrogen atom from the  $\beta$ -carbon of EB. This first C–H bond activation can be triggered by either heat or UV light irradiation. The second C–H bond cleavage for styrene production is the rate-determining step, which requires thermal excitation. This work depicts the stepwise reaction mechanism of EB dehydrogenations on TiO<sub>2</sub> unambiguously, and it may render new opportunities for developing active catalysts in the selective conversion of EB to styrene at mild conditions.

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#### Author Contributions

◆(H.P.L., Z.J.W., H.C.W., and J.Z.G.) These authors contributed equally to this work.

#### **Author Contributions**

Z.B.M, X.M.Y., and M.H.P. conceived and designed the experiments. Z.J.W., H.C.W., and Q.G. performed STM experiments. H.P.L. and Y.X. conducted thermal reaction. H.P.L. performed DFT calculations. Z.J.W., H.C.W, J.Z.G, Z.B.M., H.P.L., Q.L., and M.H.P. analyzed the data, and H.P.L. wrote the manuscript with the help of others. All the authors discussed the results and commented on and proofread the manuscript.

#### Notes

The authors declare no competing financial interest.

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