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Molecular Hydrogen Formation from Proximal Glycol Pairs on TiO_2(110)

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Supporting Information

ABSTRACT: Understanding hydrogen formation on TiO_2 surfaces is of great importance, as it could provide fundamental insight into water splitting for hydrogen production using solar energy. In this work, hydrogen formation from glycols having different numbers of methyl end-groups has been studied using temperature-programmed desorption on reduced, hydroxylated, and oxidized rutile TiO_2(110) surfaces. The results from OD-labeled glycols demonstrate that gas-phase molecular hydrogen originates exclusively from glycol hydroxyl groups. The yield is controlled by a combination of glycol coverage, steric hindrance, TiO_2(110) order, and the amount of subsurface charge. Combined, these results show that proximal pairs of hydroxyl-aligned glycol molecules and subsurface charge are required to maximize the yield of this redox reaction. These findings highlight the importance of geometric and electronic effects in hydrogen formation from adsorbates on TiO_2(110).

The technological importance of TiO_2 has driven cutting-edge research with the aim of understanding the elementary steps that underlie catalytic and photocatalytic reactions on this material.[1−5] In this context hydrogen, as a promising source of clean, renewable, and environmentally friendly energy, is of great interest.[2,6−8] As such, understanding the factors that control its formation in the thermal and photocatalytic conversion of water and organics is of critical importance. While a significant effort has been devoted to this subject, the mechanism of hydrogen formation on TiO_2 is far from understood.

For catalytic and photocatalytic studies in particular, the most stable TiO_2 surface, rutile TiO_2(110), has served as a prototypical model.[4,5] When stoichiometric or slightly reduced, the surface is unreconstructed and composed of alternating 5-fold-coordinated Ti^{4+} (Ti_{5c}) and bridging oxygen (O_b) rows. A small fraction of bridging oxygen vacancy defects (V_O's) that form as a consequence of TiO_2 bulk reduction during ultrahigh vacuum (UHV) preparation, play an important role in determining the surface reactivity of TiO_2(110).[1,4]

Water and alcohols have been thoroughly investigated on TiO_2(110) due to their importance as models in studies of photocatalytic water splitting and photo-oxidation of organic contaminants.[1−5] Both water and alcohol molecules initially dissociate at a V_O site filling it with a hydroxy (HO_b) and/or alkoxy group, respectively, and splitting hydrogen that forms another HO_b group.[9−13] Upon heating to ∼500 K, the resulting HO_b's recombine with another HO_b or an alkoxy to produce a water or an alcohol molecule, respectively.[14−18] For alcohols, the majority of alkoxy species (except for methanol which recombinatively desorbs) undergo dehydration to alkenes and water.[15−18] As a consequence, molecular hydrogen desorption from alcohols and water on TiO_2(110) has not been generally observed.[15−21] In line with these observations, theoretical calculations demonstrate that the kinetic barrier for H_2 recombinative desorption from HO_b sites on TiO_2(110) is considerably higher than the barrier for water formation.[20,21] However, in a recent temperature-programmed desorption (TPD) study,[22] Xu *et al.* reported that D_2 is formed as a minor product via thermal recombination of the D atoms on O_b sites from photocatalysis of methanol. Interestingly, hydrogen desorption between 375 and 500 K was also observed in our recent study of ethylene glycol (EG) reactions on TiO_2(110).[23]

Molecular hydrogen evolution from EG on TiO_2(110) was first observed in a study of ethanol, *n*- and 2-propanol, EG, and diethyl ether via TPD and X-ray photoelectron spectroscopy (XPS).[24] Subsequent detailed quantitative investigations with different isotopes (i.e., $HO(CH_2)_2OH$, $DO(CH_2)_2OD$, and $HO(CD_2)_2OH$) demonstrated that the observed hydrogen originates solely from hydroxyl groups and that high EG coverages are required for its formation.[23] While at low coverages, ethylene and water were identified as the only products, at saturation coverage both ethylene + water and acetaldehyde + hydrogen were observed. Total product yield of carbon-containing products at saturation coverage was determined to be ∼0.5 monolayer (ML), which clearly shows that the reactions proceed not only at V_O defect sites but also on the Ti_{5c} rows.

In this study, we systematically investigate hydrogen formation from a series of glycols with different steric constraints on differently prepared TiO_2(110) surfaces in order to further understand hydrogen formation from glycols, and polyols in general. We find that hydrogen formation is dramatically attenuated for glycols with methyl end-groups shielding the hydroxyl functional groups. Further, hydrogen formation is not observed on disordered or oxidized TiO_2(110). These results suggest that on TiO_2(110), pairs of aligned glycol molecules with hydroxyl groups in close proximity, together with subsurface charge are required to carry out this redox reaction.

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The experiments were carried out in a UHV molecular beam surface scattering apparatus (base pressure < 7×10^{-11} Torr) described previously.[16,25] A rutile $TiO_2(110)$ crystal ($10 \times 10 \times 1$ mm^3, Princeton Scientific) was cleaned by cycles of Ne^+ sputtering and annealing to 850−900 K in UHV until impurities were undetectable in Auger electron spectra. The surface prepared in this way (referred to as *r*-$TiO_2(110)$) contained ∼5% V_O defects as determined by H_2O TPD.[14,26] Additionally, hydroxylated (*h*-$TiO_2(110)$) and oxidized (*o*-$TiO_2(110)$) surfaces were prepared by exposing *r*-$TiO_2(110)$ to D_2O at 400 K, and to O_2 at 70 K, followed by annealing to 300 K, respectively.[27,28] All glycols (ethylene glycol, 1,2- and 1,3-propylene glycols, 2,3-butylene glycol, 2,3-dimethyl-2,3-butylene glycol) used in this study were obtained from Sigma-Aldrich and transferred into flasks with baked molecular sieves. The glycols were purified by pumping at room temperature, and their temperature during the dose was stabilized in a water bath. The glycols were dosed onto the various $TiO_2(110)$ surfaces using an effusive molecular beam. TPD measurements (ramp rate of 1 K/s) were performed using a quadrupole mass spectrometer (UTI).

To unambiguously determine the origin of hydrogen (O−H vs C−H), we employ OD-labeled glycols and monitor the D_2 signal during the TPD experiments. Since not all OD-labeled glycols are commercially available we prepared them directly on $TiO_2(110)$ using an H/D exchange procedure as described in the Supporting Information (SI). The viability of this procedure has been confirmed by comparing the TPD spectra from the isotopically exchanged 1,2-propylene glycol (1,2-PG) with those of commercially available OD-labeled 1,2-PG (Figure S1, SI). The use of OD-labeled glycols further allows us to overcome the experimental difficulties associated with high H_2 background during TPD due to H_2 desorption from a closed-cycle He-cryostat cooled manipulator.[23]

Figure 1a shows the coverage-dependent D_2 TPD spectra from OD-labeled ethylene glycol ($DO(CH_2)_2OD$), 1,3-propylene glycol ($DO(CH_2)_3OD$), 1,2-propylene glycol ($DOCH_2CH(CH_3)OD$), 2,3-butylene glycol ($DOCH(CH_3)$-$CH(CH_3)OD$), and 2,3-dimethyl-2,3-butylene glycol ($DOC(CH_3)_2C(CH_3)_2OD$) on *r*-$TiO_2(110)$. Other products include water and a broad range of carbon-containing species. While the discussion of the carbon-containing products for all employed glycols is beyond the scope of this report, generally alkenes are observed at low coverages, and both alkenes and aldehydes/ketones are seen at high coverages. For EG, all the products and their coverage dependences were discussed in detail in our prior publication[23] and are also summarized in Figure S2 in SI. Further, since D_2 desorption occurs at lower temperatures than desorption of any carbon-containing products (see data for EG[23] in Figure S2, SI), we believe that D_2 formation is largely decoupled from the formation of carbon-containing products at higher temperatures.

The selected sequence of glycol molecules allows us to explore how the methyl end-groups that surround the hydroxyl functional groups affect D_2 formation. Figure 1a shows that for each glycol molecule. With the exception of 2,3-dimethyl-2,3-butylene glycol, the amount of desorbing D_2 is strongly dependent on the coverage. While at low coverages (<0.25 ML), D_2 is practically absent, as the coverage increases to 0.5−1 ML, D_2 is observed for all glycols except 2,3-dimethyl-2,3-butylene glycol. As further discussed below, the absence of D_2 for 2,3-dimethyl-2,3-butylene glycol throughout the whole coverage range is a result of the steric hindrance introduced by

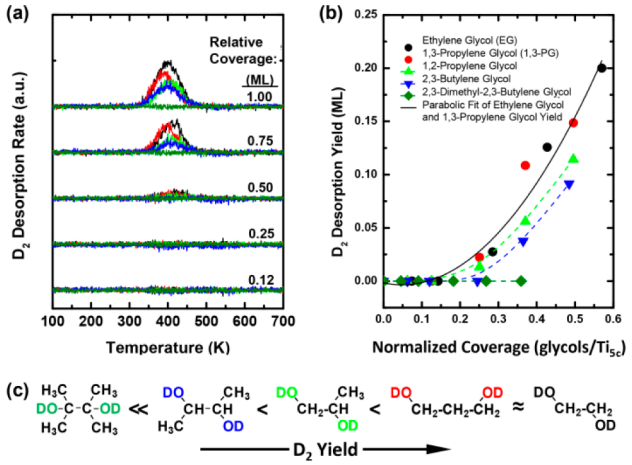

Figure 1. (a) Coverage-dependent TPD spectra of D_2 (m/z = 4 (D_2^+)) following ethylene glycol (black), 1,3-propylene glycol (red), 1,2-propylene glycol (green), 2,3-butylene glycol (blue), and 2,3-dimethyl-2,3-butylene glycol (olive) doses listed in the figure. For comparison, all OD-labeled glycols used in these experiments were prepared directly on $TiO_2(110)$ using an H/D exchange procedure described in SI. Saturation coverages (defined as 1 monolayer (ML)) correspond to the glycol exposures that saturate the high temperature TPD peak from the parent glycol molecules (see Figure S3, SI). (b) Coverage-dependent D_2 desorption yields determined from (a). To obtain normalized glycol coverages (glycol molecules per Ti_{5c} site), we normalized each coverage in (a) using the corresponding C 1s XPS peak areas of the C−OH moieties (see Figures S4 and S5 in SI for details) and employed the known saturation coverage of methanol (0.77 methanol/Ti_{5c}) as a reference.[29] (c) Schematic structures of studied glycols in the order of increasing D_2 yield.

four $-CH_3$ end-groups that surround the hydroxyl functional groups. The D_2 desorption peaks for the remaining four glycols extend from 375 to 500 K with the peak area increasing and peak maximum shifting slightly to lower temperature with increasing initial glycol coverage. The fact that the desorption temperatures are the same for all the glycols indicates that the rate limiting step is identical. As the coverage of glycols on Ti_{5c} rows reaches saturation, D_2 desorption saturates as well (spectra above saturation coverages not shown).

The integrated D_2 yields from Figure 1a are displayed as a function of normalized glycol coverage in Figure 1b. To compare the relative D_2 yield for the same number of adsorbed glycol molecules, we normalized each glycol coverage from (a) using the corresponding C 1s XPS peak area for the C−OH moieties (see Figures S4 and S5 in SI for details) and the known saturation coverage of methanol (0.77 methanol/Ti_{5c}).[29] As expected, the normalized saturation coverages decrease with increasing number of methyl end-groups in the glycols, and the normalized saturation EG coverage of 0.57 EG/Ti_{5c} is in reasonable agreement with the saturation coverage of 0.43 EG/Ti_{5c} determined previously.[23] Further, our previous EG study has shown that at saturation coverage, one D_2 is obtained on average per every two adsorbed EG molecules.[23] This D_2 yield is used to calibrate the absolute D_2 yields for other glycols in Figure 1b.

The integrated yields for all the glycols exhibit similar, superlinear dependences on coverage. In our previous study of EG we noted that neighboring Ti_{5c}-bound EG molecules may be required for the D_2 formation.[23] For spatially random adsorption on the Ti_{5c} rows, the coverage of EG pairs and hence D_2 yield should scale with the coverage squared. To see

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whether this is indeed the case we fit the data for EG to a parabolic functional form. Generally a good fit is obtained as illustrated by the solid black line shown in Figure 1b.

The quadratic yield dependence suggests that D_2 formation requires the proximal location of OD from aligned glycols. With the above picture in mind, the D_2 yields from different glycols can be compared (Figure 1c). The simplest comparison can be made for ethylene glycol and 1,3-propylene glycol. As both OD groups are primary in both molecules, a similar yield can be expected. Indeed, the D_2 desorption yields from ethylene glycol and 1,3-propylene glycols are identical within the uncertainty of the measurement. Further, the trends in D_2 yield can be evaluated as a function of increasing steric hindrance introduced by the $-CH_3$ end-groups by following the sequence of ethylene glycol analogues, i.e., 1,2-propylene glycol ($-CH_3$ at one end), 2,3-butylene glycol ($-CH_3$ on both ends), and 2,3-dimethyl 2,3-butylene glycol (two $-CH_3$ on both ends). This is schematically illustrated in Figure 2 for the case of 1,2-PG

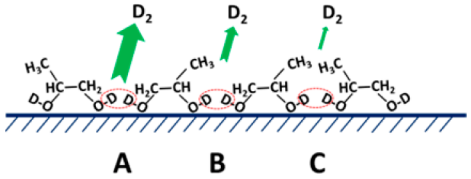

Figure 2. Three possible configurations of 1,2-propylene glycol molecular pairs on $TiO_2(110)$. From A to C, the steric hindrance increases, while D_2 formation probability decreases.

where three possible paired configurations can be envisioned. As suggested by the experimental data (Figure 1), $-CH_3$ end-groups decrease the probability of an efficient interaction between the hydroxyl groups of neighboring glycol molecules and reduce the D_2 yield. Accordingly, the saturation D_2 yield decreases from 0.20 ML for ethylene glycol to 0.11, 0.09, and finally to 0 for 1,2-propylene glycol, 2,3-butylene glycol, and 2,3-dimethyl 2,3-butylene glycol, respectively. The observed glycol dependences indicate that D_2 is formed directly from two neighboring OD species rather than being a result of recombination of deuterium diffusing on Ti_{5c} rows.

To further test the hypothesis that D_2 is being formed from pairs of neighboring glycol molecules bound on Ti_{5c} rows, we examined D_2 formation on $TiO_2(110)$ disordered by gentle sputtering (~2 ML of Ne^+). In accord with the steric hindrance arguments presented above, disordered $TiO_2(110)$ is expected to prevent the formation of proximal pairs of hydroxyl groups from aligned glycol molecules. Figure 3 shows the effect of Ne^+-sputtering on D_2 formation on the surfaces saturated with EG and 1,2-PG. Consistent with the expectations, D_2 is almost completely suppressed for EG and cannot be detected for 1,2-PG. However, after annealing to 870 K, surface order is restored, and the D_2 yield is also recovered. These results provide additional evidence for the importance of the proper alignment of OD groups of neighboring glycols for D_2 formation. Previous studies have also shown that reactions between two neighboring alcohols are completely suppressed on Ne^+-sputtered $TiO_2(110)$.[30]

Since D_2 formation results from a redox reaction that requires transfer of electrons from $TiO_2(110)$ to the adsorbed glycol molecules, we have investigated the role the availability of subsurface charge plays in the reaction. To this end, saturation coverages of OD-labeled EG (Figure 4a) and 1,2-PG

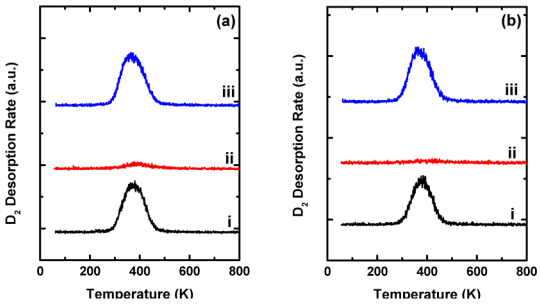

Figure 3. Effects of Ne^+ sputtering (~2 ML of Ne^+ at 1.5 kV) of clean $TiO_2(110)$ on D_2 formation from ethylene (a) and 1,2-propylene (b) glycols. Saturation coverages of OD-labeled EG and 1,2-PG were dosed at 80 K. (i) Ordered $TiO_2(110)$ before sputtering; (ii) after sputtering; (iii) sputtered and annealed to 870 K.

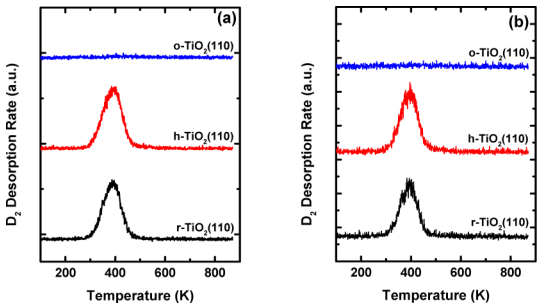

Figure 4. TPD spectra of D_2 from ethylene (a) and 1,2-propylene (b) glycols on *r*-, *h*-, and *o*-$TiO_2(110)$. Saturation coverages of OD-labeled EG and 1,2-PG were dosed at 80 K.

(Figure 4b) were dosed at 80 K on three differently prepared surfaces, i.e., *r*-$TiO_2(110)$, *h*-$TiO_2(110)$, and *o*-$TiO_2(110)$. For both glycols, D_2 TPD peaks from *h*- and *r*-$TiO_2(110)$ are nearly identical, suggesting that hydroxylation does not influence D_2 formation. Interestingly, on *o*-$TiO_2(110)$, D_2 formation is completely suppressed for both EG and 1,2-PG.

These results can be interpreted in light of what is known about the effect of surface treatments on the charge state of the $TiO_2(110)$ surface.[4] Both photoemission spectroscopy[31] and electron energy loss spectroscopy[32] studies have shown that both *r*- and *h*-$TiO_2(110)$ exhibit essentially the same defect-related electronic states. In contrast, the oxidation of $TiO_2(110)$ is known to remove these states.[31] Furthermore, in a recent study[27] Petrik *et al.* demonstrated that the amount of charge associated with the surface defects determines the amount of chemisorbed O_2, and is equivalent on both *r*-$TiO_2(110)$ and *h*-$TiO_2(110)$. Similarly, D_2 formation from the glycol OD groups on *r*- and *h*-$TiO_2(110)$ follows the same trend.

While for *o*-$TiO_2(110)$, the oxygen adatoms left on Ti_{5c} rows[33,34] are expected to serve as a barrier for the formation of glycol pairs, such a small amount (~5%) should not significantly suppress D_2 formation. A more likely origin of the complete suppression of D_2 production stems from the electron scavenging properties of O_a's.[2,31,35] As a result, on *o*-$TiO_2(110)$ the defect electrons become unavailable to adsorbed glycol molecules, preventing the redox reaction leading to D_2. These results clearly show that subsurface charge is required in D_2 formation.

The chemical insight derived from the glycol studies presented here should be also applicable to alcohol reactions on $TiO_2(110)$. Surprisingly, hydrogen is generally not

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observed[15−18] and/or represents only a minority product.[22] This can be understood upon closer inspection. From Figure 1a, D_2 desorption peaks at ∼400 K. For alcohols, the desorption from Ti_{5c} sites is usually maximized between 280 and 350 K,[29] at least 50 K lower than the temperature of hydrogen formation. This means that at the temperature of hydrogen formation, most of the alcohol molecules have already desorbed, and only alkoxy species formed by alcohol dissociation on V_O sites are present. As such, the probability of having two neighboring Ti_{5c}-bound alcohol molecules at temperatures required for H_2 formation is negligible. In contrast, the glycol molecules with two hydroxyl groups bind more strongly with TiO_2(110) and hence desorb at a much higher temperature than alcohols (see Figure S3 in SI). More importantly, the fraction of glycols that desorb intact is small (∼20% for EG) as the majority is being converted to products.[23] Therefore, there is sufficient coverage of glycols on TiO_2(110) at ∼400 K for the formation of two neighboring glycol species and D_2.

In summary, we have shown that molecular hydrogen formation from glycols on TiO_2(110) is dictated by many factors, that include glycol coverage, steric constraints of glycol molecules, surface order, and the charge state of TiO_2(110). Hydrogen formation is only observed at high glycol coverages. Increasing the steric hindrance of glycols is found to inhibit and eventually eliminate hydrogen formation. Damaging the surface order or scavenging the available surface charge of TiO_2(110) are also shown to completely suppress hydrogen formation. These findings provide strong evidence that hydrogen formation results from the bimolecular reaction between two hydroxyl groups of neighboring Ti_{5c}-bound glycols, and that the redox reaction is driven by defect electrons of TiO_2(110).

■ ASSOCIATED CONTENT

Supporting Information

Preparation procedure for OD-labeled glycols; TPD spectra from TiO_2(110) saturated by commercially available and H/D-exchanged 1,2-PG; TPD spectra of products following 0.06 and 0.57 ML EG dose; TPD spectra of parent glycol molecules; C 1s XPS spectra for glycol saturation coverages; D_2 desorption yields as a function of glycol coverages. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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