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Research Highlights

Alcohol Chemistry in Rutile TiO_2(110): The Influence of Alkyl Substituents on Reactivity and Selectivity

YK Kim,[a] BD Kay,[b] JM White,[a] and Z Dohnàlek[a]

(a) *University of Texas at Austin, Austin, Texas*
(b) *Pacific Northwest National Laboratory, Richland, Washington*

TiO_2 is widely used as a catalyst and may provide a pathway for the use of solar radiation as a viable source of clean energy. This work is a detailed study of the reaction mechanisms for the dehydrogenation reaction of alcohols on TiO_2(110). This knowledge will increase our fundamental understanding of elementary surface reactions and may lead to improvements and new applications in heterogeneous catalysis.

Many reactions on solid surfaces (e.g., oxides) occur on defect sites. On prototypical rutile TiO_2(110) surfaces, there is direct scanning tunneling microscopy (STM) evidence that bridge bonded oxygen vacancies (BBOVs) are sites for dissociation of oxygen, water, and alcohols. In the surface science and catalysis literature involving alcohol, chemistry on TiO_2, dehydration to alkenes above 500 K is well established while dehydrogenation to aldehydes or ketones and reformation of the dosed alcohols are less well established. The chemical pathways leading to these products are typically described terms of paths requiring BBOVs. However, the inability to control surface order and BBOV concentration may account for reported variations in temperature-programmed desorption (TPD) profiles of alcohol dehydration, making it difficult to establish unambiguous connections between catalytic dehydration activity and the local surface structure of TiO_2(110).

As part of a research program to establish direct atomic-level descriptions by combining STM and reaction rate measurements for oxygenates on oxides, we have recently reported on the ensemble average surface chemistry of three different isotopically labeled 2-propanols dosed at 100 K on TiO_2(110). For the first time, a low-temperature (LT) dehydrogenation path (300-450 K) was found to accompany the well-established high-temperature (HT) path ($T >$ 450 K). While surface structure is one key, variations with the alcohol are also expected and have been reported; while dehydration typically dominates, dehydrogenation contributes more for primary alcohols. The present study was motivated by a desire to determine the detailed roles played by the alkyl substituents on the accessibility of the LT and HT channels and on the dehydration selectivity. The inductive and steric effects of alkyl substituents are the concepts commonly used to understand the trends in the reactivity of similar molecules in homogeneous organic chemistry (e.g., in liquids). Here,

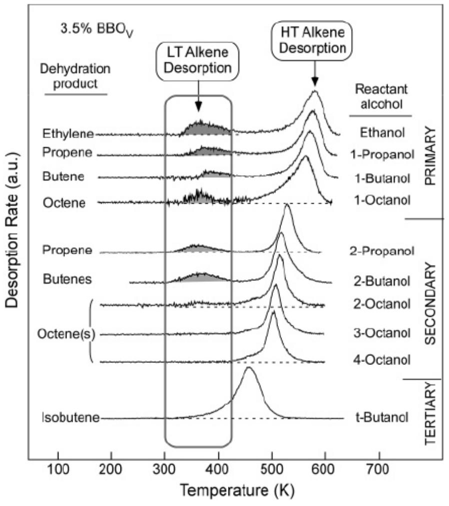

Figure 1. *TPD spectra of alkenes from 10 alcohols dosed on TiO_2^-(110) at 100 K grouped as primary, secondary, and tertiary. The net alkene desorption spectra (shown) were obtained by subtracting the fragmentation contributions of molecular alcohol. The 27 and 41 amu were used for ethylene and propene, respectively, and 56 amu was used for butenes and octenes. The alcohol dose was set to 1 ML, and all spectra were normalized to the HT alkene desorption peaks.*

we show that similar concepts can be successfully applied to understand the heterogeneous reactions at gas-solid interfaces. In this work, we report the details of the LT and HT reaction paths for primary, secondary, and tertiary alcohols for 100 K doses on well-ordered $TiO_2(110)$ with a reproducible, relatively small BBOV concentration (3.5%).

With the above picture in mind, Figure 1 displays the alkene TPD spectra for 1 ML of 10 different alcohols deposited on $TiO_2(110)$. In the LT region, seven of the 10 (ethanol, 1- and 2-propanol, 1- and 2-butanol, and 1- and 2-octanol) exhibit intensity, whereas the other three (3- and 4-octanol, and *t*-butanol) do not. When the LT channel is present, the peak temperature shows no systematic variation with alcohol structure. On the other hand, the HT channel is observed for all 10 alcohols and varies systematically with two properties of the dosed alcohol. First, the HT peak positions group together; primary alcohols are systematically higher by 50-60 K than the secondary alcohols which are, in turn, higher by another 50-60 K than the tertiary alcohol. Within each grouping, the production rate maximum drops 10-20 K as the chain lengths increase. The HT shifts are explained in terms of inductive electronic effects of the alkyl groups; the latter are described empirically using the Taft parameters of organic reaction chemistry.

The variations in LT alkene production confirm effects related to the number of carbon atoms in the alkyl chains. For primary alcohols. the low-temperature channel is active for all chain lengths studied (up to C8). For *t*-butanol, there is no evidence for LT alkene production. For secondary alcohols, alkene production is observed, except if there is no CH_3 attached to the alpha carbon.

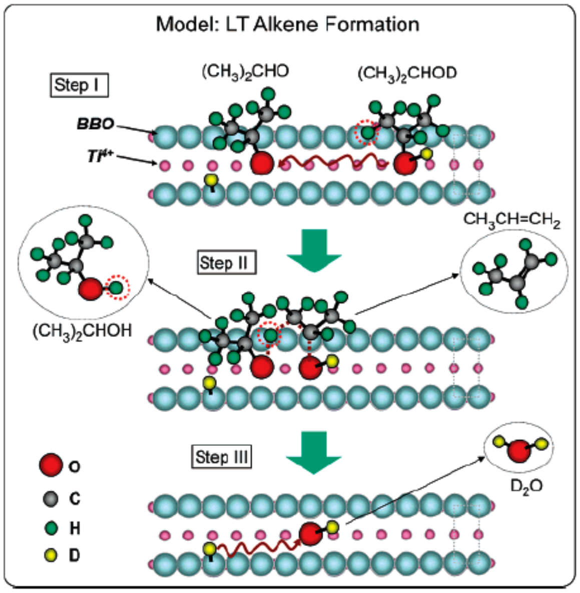

Figure 2. *Schematic of proposed LT dehydration mechanism. The key intermediate is a complex (Step II) formed by interaction of an oriented alkoxide with an oriented chemisorbed alcohol (Step I). There is a concerted rearrangement that involves beta-H, in the case shown on* CH_3*, coupling to the alkoxide oxygen and simultaneous cleavage of the C-O bond of the chemisorbed alcohol. Step III illustrates the final recombinative desorption of* D_2O*.*

Based on a series of experiments, we have developed a mechanism for the LT reaction pathway. The LT dehydration pathway is attributed to the species bound to Ti^{4+} rows. Mobility of ROH along the Ti^{4+} rows is expected and was observed in STM below the temperature where this desorption commences. The mechanism, illustrated in Figure 2, involves a mobile and oriented, but undissociated, alcohol molecule that undergoes a 1D random walk along a given Ti^{4+} row (Step I). An encounter with 2-propoxy, also oriented, during this 1D random walk form a critical activated complex (Step II) that rearranges in the LT region to form propene and 2-propanol that desorb and a mobile OH group bound to Ti^{4+} (Step III), HO_{Ti}. Finally, in the OH groups, one on a BBO row, HO_{bb}, and the other mobile and on an adjacent Ti^{4+} row, HO_{Ti}, collide and form H_2O that desorbs leaving the O_{bb}. Thus, no net loss of lattice oxygen occurs during the reaction cycle.

The exact nature of the activated complex is not clear, but the experimental evidence suggests that it requires two oriented reactants with close proximity of their alpha and beta carbon atoms. Details of this exciting research were published in the *Journal of Physical Chemistry C.*

Citation:

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