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Inductive Effect of Alkyl Chains on Alcohol Dehydration at Bridge-bonded Oxygen Vacancies of $TiO_2(110)$

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Abstract The activation energies for alkene formation via dehydration of alcohols on bridge-bonded oxygen (BBO) vacancy sites of $TiO_2(110)$ is found to correlate with the inductive electron donating effect of alcohol alkyl groups as measured by the Taft parameter. Based on this correlation we conclude that the reaction involves a single transition state that undergoes concerted rupture of the C–O bond of the alkoxide and a C–H bond of the alkyl group attached to the β-carbon.

Keywords Alcohols · Heterogeneous catalysis · $TiO_2(110)$ · Dehydration · Oxygen vacancies

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1 Introduction

Reactivity of adsorbates with titania is typically influenced by the presence of surface oxygen vacancy defects [1–3]. For alcohols, it is well-established that their dissociation on bridge-bonded oxygen vacancies (BBO_V's) of a prototypical $TiO_2(110)$ surface proceeds via heterolytic cleavage of the RO–H bond [4, 5]. The resulting intermediates are alkoxide (RO) that fills the BBO_V and a proton that binds to a neighboring bridge-bonded oxygen (BBO) anion [6–10]. Except for methoxide, these alkoxides dehydrate at elevated temperatures (well above 300 K) via β-hydride elimination to form alkenes [6, 9, 10]. In some cases, the dehydration is accompanied by a minority dehydrogenation channel yielding aldehydes [6–9].

In homogeneous reactions, the reaction rates for a series of organic species with a common functionality, have, historically, often been correlated using empirical Taft parameters [11]. Here, we show that this correlation can be extended to a heterogeneous system, namely, a series of alkoxides, primary, secondary and tertiary, bound to a single crystal rutile surface, $TiO_2(110)$. From the linear correlation of the experimental activation energies for alkene formation with tabulated values of the Taft induction parameter, σ^* [11], we conclude that the reaction transition state connecting the adsorbed reactant, alkoxide, and the gas phase product, alkene, is a structure involving concerted elongation of the C–O bond of the alkoxide and a C–H bond of the R group attached to the β-carbon.

2 Experimental

The experiments were performed in an ultra-high vacuum (UHV) molecular beam scattering chamber (5×10^{-11}

Torr) described previously [12]. A rutile $TiO_2(110)$ single crystal ($10 \times 10 \times 1$ mm^3, Princeton Scientific) ceramic-glued on a Ta plate [6], was cleaned by repeated cycles of Ne^+-sputtering (1.5 kV, 10 μA/cm^2) at 300 K and annealing at 850–900 K (~3 min) to show a sharp 1 × 1 low energy electron diffraction (LEED) pattern and no contamination (typically K, Ca, and C) as determined using Auger electron spectroscopy (AES). H_2O TPD spectra from 1 mL of H_2O dosed on $TiO_2(110)$-1 × 1 were further used to evaluate the surface morphology [13, 14] and quantitatively determine the concentration of BBO_V sites (here 3–4%) [13, 15].

The alcohols cleaned by the freeze-pump-thaw cycles were dosed with a triply differentially pumped, quasi-effusive, 300 K molecular beam (13 mm diameter) on the $TiO_2(110)$ sample held at 100 K. Temperature programmed desorption (TPD) spectra were subsequently obtained with a line-of-sight quadrupole mass spectrometer (UTI). Repeated adsorption/desorption cycles didn't leave any carbon contamination on the TiO_2 and identical doses gave reproducible alkene yields.

3 Results and discussion

Figure 1 shows a coverage dependent series of desorption spectra for alkenes formed by dehydration of their parent alcohols dosed on $TiO_2(110)$. For all alcohols except *t*-butanol, two reaction channels, one at high temperature (HT) due to dehydration on BBO_V sites [6, 9, 10] and the other at low temperature (LT) due to dehydration on Ti^{4+} sites were observed [6]. The LT channel (300–450 K) has been discussed in detail for the case of 2-propanol in our previous publication [6] and since it is not relevant to the ideas presented here it will not be further described.

The alcohol molecules shown in Fig. 1 were selected to illustrate how both the number and length of the alkyl groups attached to the α-carbon of the alkoxy groups affect the rate of HT (480–640 K) dehydration. The HT desorption feature shifts systematically from ~640 K for ethanol (primary alcohol) to ~565 K for 2-propanol (secondary alcohol) and, finally to ~480 K for *t*-butanol (tertiary alcohol). For both primary and secondary alcohols, alkene desorption occurs at lower temperatures for alcohols with longer alkyl substituents; butenes from 1-butanol (2-butanol) desorb at 628 K (554 K), which is 5 K (16 K) lower than propene from 1-propanol (2-propanol). In this study, no chain-length comparison is made for the case of tertiary alcohols.

The effect of various alkyl groups on the activation energy, E_D, for alcohol dehydration on $TiO_2(110)$ is further analyzed in Fig. 2. We use Redhead analysis based on the experimentally observed maximum-desorption-rate temperature, T_{mdr}, from the TPD spectra in Fig. 1 to extract the activation energy, E_D, for alkene formation [16].[1] In Fig. 2, both T_{mdr} and E_D are plotted vs. tabulated Taft parameters, σ^* for the various alcohols [11]. This parameter has been extensively used to quantify the electron-donating inductive effect of the alkyl groups on the reaction rate observed in homogeneous organic reaction studies [11]. In heterogeneous reactions, the inductive effect of substituent groups has also been observed, specifically, in dehydrogenation reactions of alkoxides on ZnO-Cr_2O_3 [17], vanadia supported on ceria and titania [18], and Cu(111) [19, 20]. In these studies the Taft parameter was used to correlate the inductive effects of alkyl substituents with the activation barrier for dehydrogenation. It was concluded the transition state involves heterolytic cleavage of the α-$C^{\delta+}$–H bond [17].

Here, we use this parameter to correlate the stabilization effect of electron-donating alkyl groups with the energetic

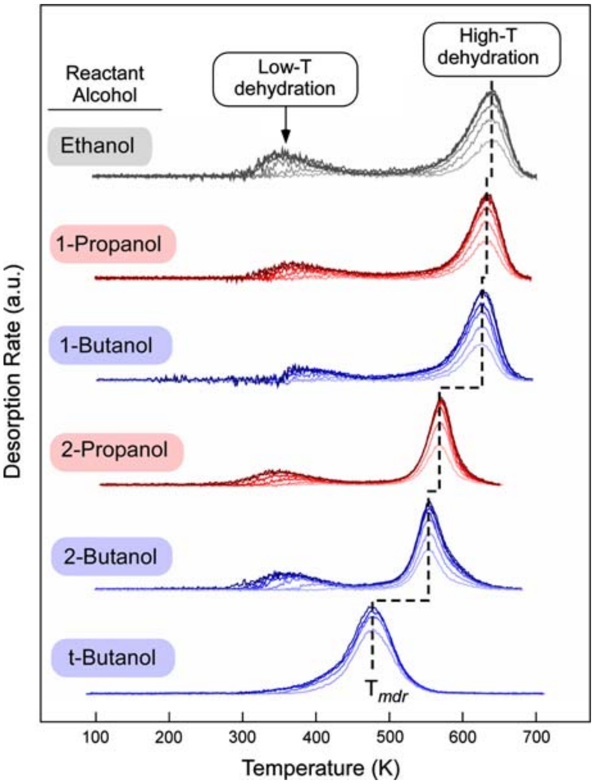

Fig. 1 Coverage dependent (0.1–1 ML) temperature programmed desorption (TPD) spectra of alkene molecules formed by dehydration of their parent alcohols dosed on $TiO_2(110)$ at 100 K. The net alkene desorption rates (R_D) were obtained by subtracting the contribution of the molecular alcohol fragments obtained from the multilayer TPD spectra of corresponding alcohols. All spectra were obtained using a linear ramp rate of 1.8 K/s and normalized to their saturation peak intensities (1 monolayer, ML)

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[1] This simplified analysis assumes a first-order reaction kinetics and a typical value of pre-exponential factor of 10^{13} s^{-1}.

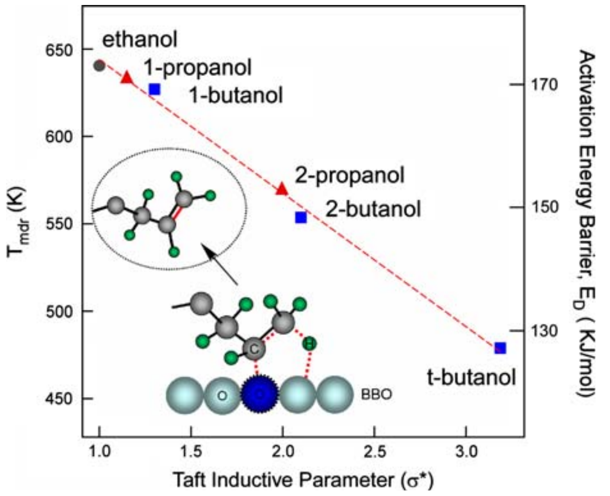

Fig. 2 Temperature of maximum desorption rate (T_{mdr}) and activation energy for alkene formation (E_D) for high-temperature dehydration of alcohols adsorbed on $TiO_2(110)$ plotted against Taft inductive parameter (σ^*) of alcohol alkyl groups.[11] The inset shows a schematic of the high-T dehydration of alkoxide bound to BBO_V. σ^* is scaled to set ethanol to 1.0

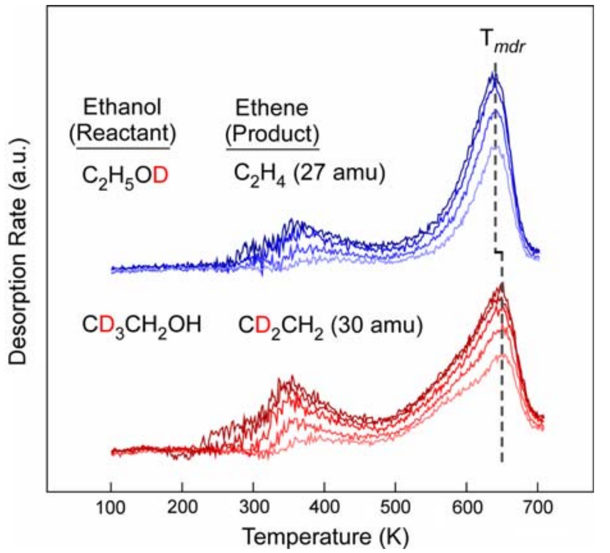

Fig. 3 Coverage dependent (0.1–1 ML) temperature programmed desorption (TPD) spectra of ethene formed by dehydration of isotopically labeled ethanol dosed on $TiO_2(110)$ at 100 K. The net ethene desorption rates (R_D) were obtained by subtracting the contribution of the ionization cracking fragments obtained from the multilayer TPD spectra of the corresponding ethanol isotopes. All spectra were obtained using a linear ramp rate of 1.8 K/s

barrier of the alcohol dehydration on BBO sites of $TiO_2(110)$. An excellent linear dependence of E_D on σ^* of the alkyl substituents is clear from the linear fit shown in Fig. 2. The heterolytic nature of the $C^{\delta+}$–O bond is expected to be enhanced at the transition state where the $C^{\delta+}\cdots O$ bond is elongated. Since σ^* is correlated with the stabilization of the positively charged carbon atom, the stabilizing effect is greater at transition state than in the adsorbed reactant. This explains why an alkyl substituent with a higher electron donating capacity (higher σ^*) results in a lower activation barrier, E_D. Thus, our data suggest that C–O bond cleavage occurs via a heterolytic mechanism; the transition state involves heterolytic $C^{\delta+}$–O bond cleavage stabilized to different degrees by the electron-donating effect of the alkyl substituents.

The nature of the transition state can be further explored by employing alcohol molecules with isotopically labeled hydrogen. In our recent study of 2-propanol on $TiO_2(110)$ [6], we have observed that the dehydration of deuterated 2-propanol ($(CD_3)_2CDOD$) to propene (C_3D_6) occurs at temperatures 8–13 K higher than that for hydrogenated 2-propanol ($(CH_3)_2CHOH$) with the significant difference in desorption rates ($k(C–H)/k(C–D) = 2.4$) at the same temperature indicating that C–H bond cleavage is also involved in the transition state. Further, exclusive formation of CD_2CH_2 from partially deuterated ethanol (CD_3CH_2OH) shown in Fig. 3 demonstrates that the dehydration proceeds via β-C–H elimination as already suggested in the literature [6, 9, 10].

As argued above, the linear dependence of E_D on σ^* is a clear indication of heterolytic bond cleavage during alcohol dehydration on $TiO_2(110)$ and as such σ^* reflects the change of charge/electron density when going from the initial to transition state. In contrast, a radical dehydration mechanism was previously proposed to explain the generally observed preference for alcohol dehydration over dehydrogenation, which is unlikely when we consider that the abstraction of α-hydrogen leading to the dehydrogenation is energetically less costly than the abstraction of β-hydrogen [9]. Based on our systematic studies of primary, secondary, and tertiary alcohols, we conclude that the preference for dehydration over dehydrogenation stems from stabilization of the transition state likely due to it's 5-membered cyclic structure involving $O\cdots C^{\delta+}–C\cdots H\cdots BBO$ as illustrated in the inset of Fig. 2.

4 Conclusions

Based on the arguments presented above, we conclude that alcohol dehydration is an E2-type reaction [21, 22] involving concerted C–H and C–O bond breaking of the alkoxy group and attendant H-BBO and C=C bond formation. Compared to the rather large effect of alkyl substituents on E_D (as much as 40 kJ/mol in Fig. 2), deuteration results in a relatively small perturbation (2–3 kJ/mol) on the overall barrier. This is expected, given the correlation (Fig. 2) between reaction energy barrier and the inductive electron donating effect (σ^*) of alkyl groups.

Within the framework of a concerted reaction, this suggests that the transition state geometry is characterized by a C–C$^{\delta+}$–O bond that is near the dissociation limit, a partially formed C=C bond and a C–H bond that is stretched toward an incipient bonding configuration with a BBO in the titania substrate.)

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References

1. Diebold U (2003) Surf Sci Rep 48:53
2. Schaub R, Thostrup R, Lopez N, Laegsgaard E, Stensgaard I, Norskov JK, Besenbacher F (2001) Phys Rev Lett 87:4
3. Lu GQ, Linsebigler A, Yates JT (1994) J Phys Chem 98:11733
4. Zhang ZR, Bondarchuk O, White JM, Kay BD, Dohnalek Z (2006) J Am Chem Soc 128:4198
5. Zhang Z, Bondarchuk O, Kay BD, White JM, Dohnalek Z (2007) J Phys Chem C 111:3021
6. Bondarchuk O, Kim YK, White JM, Kim J, Kay BD, Dohnalek Z (2007) J Phys Chem C in press
7. Kim KS, Barteau MA (1990) J Mol Catal 63:103
8. Kim KS, Barteau MA, Farneth WE (1988) Langmuir 4:533
9. Farfan-Arribas E, Madix RJ (2002) J Phys Chem B 106:10680
10. Gamble L, Jung LS, Campbell CT (1996) Surf Sci 348:1
11. Taft RW (1953) J Am Chem Soc 75:4231
12. Dohnalek Z, Kim J, Bondarchuk O, White JM, Kay BD (2006) J Phys Chem B 110:6229
13. Henderson MA (1996) Langmuir 12:5093
14. Henderson MA (2002) Surf Sci Rep 46:5
15. Henderson MA (1998) Surf Sci 400:203
16. Redhead PA (1962) Vacuum 12:203
17. Gulkova D, Kraus M (1994) J Mol Catal 87:47
18. Feng T, Vohs JM (2004) J Phys Chem B 108:5647
19. Li X, Gellman AJ, Sholl DS (2006) Surf Sci 600:L25
20. Gellman AJ (2000) Acc Chem Res 33:19
21. Baertsch CD, Komala KT, Chua YH, Iglesia E (2002) J Catal 205:44
22. Macht J, Baertsch CD, May-Lozano M, Soled SL, Wang Y, Iglesia E (2004) J Catal 227:479