Adsorption of Small Hydrocarbons on Rutile TiO₂(110)

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Abstract

Temperature programmed desorption and molecular beam scattering were used to study the adsorption and desorption of small hydrocarbons (n-alkanes, 1-alkenes and 1-alkynes of C₁-C₄) on rutile TiO₂(110). We show that the sticking coefficients for all the hydrocarbons are close to unity (> 0.95) at an adsorption temperature of 60 K. The desorption energies for hydrocarbons of the same chain length increase from n-alkanes to 1-alkenes and to 1-alkynes. This trend is likely a consequence of additional dative bonding of the alkene and alkyne π system to the coordinatively unsaturated Ti_{5c} sites. Similar to previous studies on the adsorption of n-alkanes on metal and metal oxide surfaces, we find the desorption energies within each group (n-alkanes vs. 1-alkenes vs. 1-alkynes) from Ti_{5c} sites increase linearly with the chain length. The absolute saturation coverages of each hydrocarbon on Ti_{5c} sites were also determined. The saturation coverage of CH₄, is found to be $\sim 2/3$ monolayer (ML). The saturation coverages of C₂-C₄ hydrocarbons are found nearly independent of the chain length with values of $\sim 1/2$ ML for n-alkanes and 1-alkenes and $2/3$ ML for 1-alkynes. This result is surprising considering their similar sizes.

Keywords: hydrocarbons; adsorption; desorption; temperature programmed desorption; sticking coefficient

1. Introduction

Transition metal oxides play a prominent role in materials research, especially as energy-related materials and understanding how they interact with small molecules is central to many scientific and technological challenges that include heterogeneous catalysis, adhesion, lubrication, chemical sensing, and others [1, 2]. Among oxides, the surface of rutile $\text{TiO}_2(110)$ is one of the most thoroughly studied, both experimentally and theoretically, and has served as a prototypical model for fundamental studies of reducible metal oxides [3-7]. This study details the adsorption and desorption of a series of small ($\text{C}_1\text{-C}_4$) hydrocarbons (n-alkanes, 1-alkenes, and 1-alkynes) on $\text{TiO}_2(110)$. Such studies are of critical importance as they provide quantitative information about the kinetic parameters governing the adsorption/desorption on well-defined surfaces. Such data are invaluable in the studies of more complex systems and serve as a reference for benchmarking the theoretical methods [4, 6, 8]. In addition to being of fundamental interest, hydrocarbon adsorption/desorption studies have practical implications. For example, light olefins, such as ethylene and propylene, are the feedstock employed in the production of a vast array of chemicals, and catalytic dehydrogenation of light alkanes on metals and/or metal oxides have been recognized as a favorable way to produce light olefins [9]. Further, the catalytic applications of acetylene as a feedstock for the chemical industry have also been revisited very recently [10].

The interaction of hydrocarbons with single crystal metal surfaces has been extensively studied over the past decades [2, 11-39]. The results of these studies indicate that alkanes can physisorb, chemisorb, or react with adsorbates already on the surface, depending on metal substrate, surface temperature and other experimental conditions [11-19]. While the exact adsorption energies depend on the metal and its surface structure, a linear dependence of the adsorption energy on molecular chain length is generally observed for the adsorption of short alkanes on many metal surfaces [2, 20-23, 39]. This linear increase in adsorption energy with the chain length has been interpreted in terms of bonding configurations in which the alkane chains lie parallel to the metal surface [2, 20-23]. For unsaturated hydrocarbons such as ethylene and acetylene, their adsorption on metal surfaces in general can be described within the Dewar-

Chatt-Duncanson chemisorption model, in which the bonding is formed via a π -donation from the adsorbate into empty metal-states coupled with back-donation from the metal into the empty orbital of the hydrocarbon [24-28]. This bonding configuration entails a rehybridization of the carbon atoms, which results in a C-C bond elongation and an upward “bending” of the hydrogen atoms from the surface [24-28]. Upon heating, the adsorbates undergo either desorption, decomposition or transformation to different reaction products, depending on the combination of the unsaturated hydrocarbons and the single crystal metal surfaces investigated [24, 28-38].

Compared to work on single crystal metal surfaces, only a few studies have focused on the interaction of hydrocarbons with well-defined metal oxide surfaces, despite their important role in catalytic processes. The work available in the literature in this regard has been largely limited to the adsorption of small n-alkanes (C_NH_{2N+2} , $N = 1 - 12$) on $Al_2O_3(0001)$ [40], $MgO(100)$ [41-46], and $PdO(101)$ [47-52]. Using temperature programmed desorption (TPD), Slayton *et al.* [40] first investigated the desorption of butane, hexane and octane from $Al_2O_3(0001)$ under ultrahigh vacuum (UHV) conditions, and their data suggested that the relative magnitude of molecule-surface interactions compared to molecule-molecule interactions decreases with increased chain length. To extract accurate and robust desorption kinetic parameters from the TPD data, Tait *et al.* [43] developed a rigorous inversion-optimization analysis, where the coverage dependent desorption energy is determined for a constant value of the prefactor. The prefactor is subsequently varied to minimize the difference between the coverage-dependent sets of experimentally-determined and simulated TPD spectra. In the subsequent studies, this analysis method was employed to study the desorption kinetics for a series of n-alkanes (C_NH_{2N+2} , $N = 1-10$) from $MgO(100)$ [44]. A notable finding in this work was a linear increase in the desorption energy with a small y-intercept value, along with an observed six orders of magnitude increase in prefactor with increasing the molecular chain length [44]. In contrast with the physisorption of n-alkanes on $Al_2O_3(0001)$ and $MgO(100)$ surfaces, the adsorption of n-alkanes on the late transition oxide $Pd(101)$ surface has been demonstrated to yield σ -complexes by datively bonding with the coordinatively-unsaturated Pd atoms, which act as precursors for

the C-H bond activation of the n-alkanes larger than ethane [47-52]. Recent studies have predicted that other late transition-metal oxide surfaces should exhibit high reactivity toward alkanes due to the availability of both coordinately-unsaturated metal and oxygen surface sites [47]. Among these late transition-metal oxide surfaces, RuO₂(110) is particularly interesting, because it is isostructural with rutile TiO₂(110) [53]. As such, the basic knowledge of the adsorption and desorption of small hydrocarbons on TiO₂(110) should provide a good reference point for studying their adsorption and activation on a more acidic RuO₂(110). In this regard, the adsorption of ethylene on stoichiometric RuO₂(110) has been studied by Paulus *et al.* who found that ethylene does not react with the surface and desorbs molecularly at 320 K[54]

In this work, we use TPD and molecular beam techniques to study the adsorption and desorption kinetics of a series of small hydrocarbons (C₁ - C₄) on TiO₂(110). In addition to n-alkanes (methane, ethane, propane, n-butane), we have also followed the adsorption of 1-alkenes (ethene, propene and 1-butene) and 1-alkynes (ethyne, propyne and 1-butyne) to determine the effect of carbon-carbon bond order and the molecular chain length on hydrocarbon binding. Similar to previous studies, for n-alkanes we find a linear increase in the desorption energy with chain length, *N*. For hydrocarbons of the same chain length we find that the unsaturated hydrocarbons are more tightly bound as compared to n-alkanes. This enhanced binding is most pronounced for ethene and ethyne, which at low coverages are bound 1.3 and 1.4 times more strongly than ethane. This is likely a consequence of the dative bonding of the π -system of the unsaturated hydrocarbons with the five-fold coordinated titanium sites (Ti_{5c}). For 1-alkenes and 1-alkynes, a roughly linear relationship between the desorption energy and chain length is also observed, but with a smaller slope than the n-alkanes. This suggests that the additional CH_x segments in 1-alkenes and 1-alkynes destabilize the bonding of the unsaturated carbon-carbon bond with the Ti_{5c} sites. Further, we have determined the absolute saturation coverages of each hydrocarbon on Ti_{5c} sites by employing a combination of TPD and molecular beam dosing. The results show that except for CH₄, the absolute saturation coverages of the same type of hydrocarbons (n-alkanes, 1-alkenes or 1-alkynes) on Ti_{5c} sites

are nearly independent of the chain length, and that the saturation coverages of 1-alkynes consistently exceed those of n-alkanes and 1-alkenes, contrary to what one would heuristically expect based on their similar sizes.

2. Experimental

All experiments were performed in a UHV molecular beam surface scattering apparatus with a base pressure of $< 1 \times 10^{-10}$ Torr which has been described in more detail in our previous publications [55, 56]. The rutile $\text{TiO}_2(110)$ -1 $\times$ 1 crystal ($10 \times 10 \times 1 \text{ mm}^3$) was obtained from Princeton Scientific, and mounted onto a Ta sample holder. The Ta holder was attached to a closed-cycle He cryostat for cooling to $\sim 60 \text{ K}$ and resistive heating to $> 900 \text{ K}$. The temperature was measured by a chromel-alumel (type K) thermocouple glued to the edge of the crystal.

The initial surface cleaning procedure was comprised of cycles of Ne^+ sputtering (1.5 kV, 10 μA) at 300 K and annealing at 850 $\sim$ 900 K for 10 min until a clean and ordered $\text{TiO}_2(110)$ -1 $\times$ 1 surface was obtained based on Auger electron spectroscopy (AES), X-ray electron spectroscopy (XPS), and low energy electron spectroscopy (LEED) analysis. To maintain the surface cleanliness and order, a brief, 3 min sputtering at 300 K followed by 10 min of annealing at 870 K was used on a daily basis. Reproducibility of the surface structure was further confirmed using H_2O TPD [1]. The population of bridge bonded oxygen vacancies (V_O 's) on the surface was determined to be $\sim 5\%$ based on the ratio of water recombination desorption peak at $\sim 500 \text{ K}$ to the monolayer desorption peak at $\sim 270 \text{ K}$ [1, 57].

The adsorbates studied were n-alkanes (methane, ethane, propane and n-butane), 1-alkenes (ethene, propene and 1-butene), and 1-alkynes (ethyne, propyne and 1-butyne). Methane and all 1-alkenes with research grade purity were purchased from Matheson. Ethyne (acetylene) was obtained from Oxarc with an atomic absorption grade, and all the remaining molecules were from Sigma-Aldrich with purity $> 98\%$. A flux-calibrated effusive molecular beam of the pure gas was used for dosing at normal incidence with

respect to the sample surface plane. During adsorption, the sample was held at ~ 60 K, a temperature well below the onset of the multilayer desorption of all adsorbates except methane as discussed below.

Absolute coverages for all adsorbates were defined in monolayers (ML) relative to the number of Ti^{4+} sites ($1 \text{ ML} \equiv 5.2 \times 10^{14} \text{ cm}^{-2}$) on $\text{TiO}_2(110)$. All TPD spectra were acquired using a quadrupole mass spectrometer (UTI 100C) in a line-of-sight geometry at a constant heating rate of 1 K/s. No hydrocarbon dissociation on $\text{TiO}_2(110)$ was observed as confirmed by XPS and by the excellent reproducibility of the TPD spectra upon repeated doses.

3. Results and Discussion

3.1 Sticking Coefficient Measurements

The sticking coefficients of all hydrocarbons studied here were measured by the beam reflection technique of King and Wells [58] at the base sample temperature of 60 K. A representative sticking coefficient measurement using an effusive beam of propyne at normal angle of incidence relative to surface plane is shown in Figure 1. During the sticking coefficient measurements, the mass spectrometer was positioned such that only the background pressure increase was measured (no line-of-sight contribution). The reference signal, $P_1(t)$, (solid black trace), where no molecules are retained on the surface, is obtained by holding the $\text{TiO}_2(110)$ sample temperature well-above any observed TPD features (here 500 K) [59]. At 60 K, the same incident beam produces a lower signal, $P_2(t)$, (red trace) indicating that a fraction of the molecules is being retained on the surface. This signal is well above the background and remains approximately constant as a function of time. To determine the fraction of molecules that stick on the surface one has to account for the background increase when the beam shutter is opened. This background pressure increase is mainly caused by the presence of a small effusive (nondirectional) component in the molecular beam as discussed in details in our previous studies [60, 61]. This fractional pressure increase, X , due to this effusive component is characteristic of the beam source and independent of the molecule dosed. This component can be determined for example by using a reference adsorbate

with a known sticking coefficient, S . We used water, which at $T < 90$ K has the sticking coefficient that is very close to unity, $S_{\text{TiO}_2}^{\text{H}_2\text{O}} \cong 1.0$ [59], and determined the value of X to be 10%. This background signal due to the effusive component is shown as a dotted black reference line in Figure 1. An identical value was also determined by dosing propyne on the $\text{TiO}_2(110)$ precovered with propyne multilayers. In this experiment the efficiency of the energy transfer and consequently sticking probability between the incident adsorbate and the surface is also very close to unity due to their mass match [60, 61].

Figure 1. Transient propyne pressure increase, $P(t)$, after introduction of the effusive propyne beam into the UHV chamber. The pressure increase with the $\text{TiO}_2(110)$ sample held at 60 K ($P_2(t)$, red) and 500 K ($P_1(t)$, solid black). The dotted black trace represents the pressure increase due to nondirectional component of the propyne beam. The inset shows the sticking coefficient determined at 60 K as a function of propyne coverage.

The directional components in $P_1(t)$ and $P_2(t)$ can be obtained by subtracting the non-directional component (dotted black trace, Figure 1) from $P_1(t)$ and $P_2(t)$. The sticking coefficient, $S(t)$, as a function of dose time, t , is calculated using the following expression:

$$S(t) = 1 - \frac{P_2(t) - XP_1(t)}{(1 - X)P_1(t)} = \frac{1}{1 - X} \left(1 - \frac{P_2(t)}{P_1(t)}\right)$$

The resulting coverage-dependent sticking coefficient determined using this expression is plotted as a function of propyne coverage and shown in the inset of Figure 1. The results indicate that at a base temperature of 60 K the sticking coefficient of propyne on TiO₂(110) is close to unity, even at the zero coverage limit, $S_{TiO_2}^{C_3H_4}(t=0) = 0.98$. The sticking coefficients for other hydrocarbons employed in this study were measured in a similar fashion and values close to unity were also found under our experimental conditions. As a result, the absolute coverage, θ , can be simply determined from the dose time, t , and a known beam flux, F , for our calibrated molecular beam as $\theta = F \cdot t$.

3.2 Coverage Dependent TPD Spectra

The TiO₂(110) surface is composed of rows of topographically low-lying 5-fold coordinated titanium ions (Ti_{5c}) and rows of topographically high-lying bridging oxygen ions (O_b). Additionally, as a consequence of TiO₂ bulk reduction during UHV preparation, a small fraction of the surface O_b ions is missing, forming the bridge bonded oxygen vacancies (V_O's, here ~5%). Prior TPD studies of other adsorbates (e.g. H₂O, CO₂, CO, N₂ and O₂) [59, 62-64], have shown that V_O's often represent the most stable adsorption sites where molecules can adsorb dissociatively (e.g. H₂O, O₂) and/or molecularly (e.g. CO₂) while in other cases no clear preference is observed (e.g. N₂, CO). From regular sites, the Ti_{5c} sites are generally preferred over O_b sites due to larger polarization of the molecules on the more highly charged Ti_{5c} sites.

The coverage-dependent TPD spectra from n-alkanes (methane, ethane, propane, and n-butane) on reduced TiO₂(110) are shown in Figure 2. Only a representative subset of the measured spectra is plotted for each molecule. The absolute coverages were determined using the calibrated beam fluxes [59], measured sticking coefficients, and the dose times and are referenced relative to the number of Ti_{5c} sites

(1 ML $\equiv 5.2 \times 10^{14} \text{ cm}^{-2}$). The desorption spectra for all of the alkanes have similar desorption features, we will use the methane spectra (Figure 2a) as an example to describe and assign the peaks.

Figure 2. Coverage dependent TPD spectra for (a) methane, (b) ethane, (c) propane and (d) n-butane on $\text{TiO}_2(110)$. All TPD spectra were acquired using a constant ramp rate of 1 K/s. The

assignment of TPD peaks from titanium (Ti_{5c}) sites, bridge-bonded oxygen (O_b) sites, and multilayers (M) is indicated in each panel. The red traces correspond to the saturation coverage of compressed n-alkane layers on Ti_{5c} rows (before the appearance of the TPD features from the O_b sites). The blue traces correspond to the coverages of uncompressed layers as represented by the saturation of TPD peaks from Ti_{5c} sites. The insets show the TPD area vs. n-alkane coverage, θ . The absolute coverages were determined using the calibrated beam fluxes, measured sticking coefficients, and the dose times and are referenced relative to the number of Ti_{5c} sites ($1 \text{ ML} \equiv 5.2 \times 10^{14} \text{ cm}^{-2}$).

At the lowest methane coverage of 0.1 ML, a single peak is observed in TPD at $\sim 90 \text{ K}$. Higher coverages result in the growth of the peak intensity and a slight shift of its maximum to lower temperatures. The peak saturates at $\sim 0.6 \text{ ML}$ (blue trace, Figure 2a) and exhibits a maximum at 85 K . Further coverage increase above 0.6 ML initially results in a development of the shoulder ($\theta = 0.71 \text{ ML}$, red trace) on a low temperature side of the 85 K peak and subsequently ($\theta > 0.71 \text{ ML}$) leads to the development of a low temperature peak at $\sim 70 \text{ K}$. The highest attainable coverage for methane at the base temperature of 60 K is $\sim 1.22 \text{ ML}$.

Additional small high temperature peak develops at high coverages above 100 K . This peak has been determined to be an artifact due to minor adsorption on the sample holder. This assertion is supported by several observations; (a) The peak is not observed at lowest coverages despite that it should fill first (if from the surface) as it would correspond to most strongly bound methane, (b) The peak increases continuously without saturation with increasing n-alkane dose indicating that it does not correspond to desorption from the low coverage ($\sim 0.05 \text{ ML}$) V_o sites, (c) The peak grows more rapidly when the sample is somewhat misaligned (3-5 mm) off the beam axis. Additional evidence supporting this conclusion comes from coadsorption experiments, which show that that this feature does not change even when a more strongly bound species such as water is adsorbed (see Figure S1, Supporting Information (SI)) [64].

By analogy with other adsorbates (e.g. H_2O , CO_2 , CO , N_2 and O_2) studied previously on $\text{TiO}_2(110)$ [59, 62-64], we assign the ~ 85 K high temperature peak (labeled Ti_{5c}) to the desorption of methane from the Ti_{5c} sites and the ~ 70 K low temperature peak (labeled O_b) to the desorption from bridge-bonded oxygen, O_b , sites. The plateau between the peaks results from compression of the molecules on the Ti_{5c} sites which collectively leads to their less favorable binding configurations. This compression results in a shift of the peak leading edge to lower temperature without further growth of the peak intensity [59, 65]. The compression continues until the chemical potential of the adsorbed molecules on Ti_{5c} rows reach that of the molecules in the second layer adsorbed on O_b rows. As the coverage is increased further, the peak from the O_b sites emerges.

The coverage-dependent TPD spectra of ethane (Figure 2b), propane (Figure 2c) and n-butane (Figure 2d) develop in a similar fashion and exhibit analogous features to those of methane. Stronger van der Waals interactions allow us to also condense multilayers which results in the appearance of an additional peak on the low temperature end of the spectra (labeled M). These multilayer features grow without saturation as the dose is increased.

Generally, the TPD peak maxima shift to higher temperatures for both Ti_{5c} - and O_b -bound n-alkanes as their length, N , increases. This is a consequence of increasing van der Waals interactions as discussed in the introduction and as observed previously on many metal and metal oxide surfaces [20-23, 39, 44]. Specifically, the TPD peak temperatures for the molecules desorbing from the Ti_{5c} sites increase from 85 K for methane to 116, 140, and 164 K for ethane, n-propane, and n-butane, respectively. Analogously, the peak temperatures on the O_b sites increase from 68 K for methane to 88, 104, and 122 K for ethane, n-propane, and n-butane, respectively. Larger differential shifts on Ti_{5c} sites (~ 25 K/ N) as compared to those on O_b sites (~ 18 K/ N) are a consequence of larger polarization of the n-alkanes on the more highly charged Ti_{5c} sites. A similar increment to that observed on O_b sites is also seen for the onset of multilayer desorption (~ 15 K/ N) in accord with that (~ 16 K/ N) previously determined for the desorption of n-alkanes from multilayers on $\text{MgO}(100)$ [44]. This similarity indicates that the interactions of the n-alkanes with

the O_b sites are relatively weak and approach the van der Waals interactions in the condensed phase. The observed trends are summarized in Table 1.

The integrated TPD peak areas as a function of n-alkane coverage are plotted as insets in Figure 2. The integrals clearly show that the TPD peak area increase linearly with coverage and pass through the origin of each plot. The absolute n-alkane coverages on the x axes were derived from the beam fluxes, measured sticking coefficients, and the dose times ($\theta = F \cdot S \cdot t$). The observed linear relationships confirm the absence of any irreversible reactions during the TPD experiments.

Number of Carbons, N	Peak Desorption Temperatures [K]								
	n-alkanes			1-alkenes			1-alkynes		
	M	O _b	Ti _{5c}	M	O _b	Ti _{5c}	M	O _b	Ti _{5c}
1	-	68	85						
2	80	88	116	76	83	139	86	/	148
3	94	104	140	96	107	181	109	/	169
4	111	122	164	107	124	192	116	/	183

Table 1. TPD peak temperatures for n-alkanes, 1-alkenes, and 1-alkynes desorbing from Ti_{5c} and O_b, sites on TiO₂(110) and from their multilayers, M. We were unable to determine the 1-alkynes desorption temperatures from O_b sites due to peak overlap with that from the multilayers.

The TPD spectra from small 1-alkenes (ethene, propene, and 1-butene) on TiO₂(110) are shown in Figure 3. A similar coverage dependent progression as for n-alkanes is observed with 1-alkenes initially populating the Ti_{5c} sites, followed by O_b sites, and finally multilayers. Specific V_O-related TPD features are not observed. Several notable differences, as compared to the n-alkanes, can be seen. The TPD peak desorption temperatures of 1-alkenes from Ti_{5c} sites are significantly higher (20 - 40 K) as compared to n-alkanes with the same number of carbon atoms (see Table 1). The origin of this substantial increase (20-30%) likely stems from dative interactions of the alkene π system of the C = C segment with the coordinatively unsaturated Ti_{5c} sites as further discussed below. Additionally, there is a significant

increase in the width of the Ti_{5c} -related TPD peaks, in particular for propene and 1-butene. It is possible that this broadening is due to a decrease in the optimum alignment of the C=C bond with the underlying Ti_{5c} sites with increasing coverage. As evidenced by the linear relationship between the TPD peak areas and 1-alkene coverages (insets of Figure 3) there is no reaction between the 1-alkenes and $\text{TiO}_2(110)$.

Figure 3. Coverage dependent TPD spectra for (a) ethene, (b) propene, and (c) 1-butene on $\text{TiO}_2(110)$. The assignment of TPD peaks from Ti_{5c} sites, O_b sites, and multilayers (M) is indicated in each panel. The red traces correspond to the saturation coverage of compressed 1-alkene layers on Ti_{5c} rows (before the appearance of the TPD features from the O_b sites). The blue traces correspond to the coverages of uncompressed layers as represented by the saturation of

TPD peaks from Ti_{5c} sites. The insets show the TPD area vs. 1-alkene coverage, θ . The absolute coverages were determined using the calibrated beam fluxes, measured sticking coefficients, and the dose times and are referenced relative to the number of Ti_{5c} sites ($1 \text{ ML} \equiv 5.2 \times 10^{14} \text{ cm}^{-2}$).

The TPD spectra for small 1-alkynes (ethyne, propyne, and 1-butyne) on $\text{TiO}_2(110)$ are shown in Figure 4. A similar coverage dependent progression as for n-alkanes and 1-alkenes is observed. Initially the Ti_{5c} sites are populated showing a very broad feature for ethyne and rather sharper features for propyne and 1-butyne. Since a distinct peak is not observed in the coverage-dependent ethyne TPD spectra, we have not defined the coverage corresponding to the uncompressed ethyne on Ti_{5c} sites (blue TPD spectra for other molecules). The dramatic continuous coverage-dependent shift to lower temperatures observed for ethyne from very low coverages is rather puzzling. Interestingly, while the ethyne peak desorption temperature is about 10 K higher than that of ethene, the peak temperatures of propyne and 1-butyne are ~ 10 K lower than those of propene and 1-butane (see Table 1). The origin of these subtle changes cannot be assessed based on our experiments and points to the need for future theoretical studies. No distinct features can be correlated with the presence of V_O 's on the surface. Further, the TPD peak from the O_b sites cannot be clearly isolated from the multilayer desorption peaks as the coverage is increased above the saturation of the Ti_{5c} sites. This is likely a consequence of higher peak temperatures for the desorption from alkyne multilayers (lower vapor pressures) as compared to those from n-alkanes and 1-alkenes with the same N in accord with their higher enthalpies of sublimation (e.g., 21.9 - 23.5 kJ/mol for ethyne vs. 20.5 - 22.6 and 15.3 - 18.4 for ethane and ethene, respectively [66]). Similar to n-alkanes and 1-alkenes, no reaction is observed during the TPD experiments, as evidenced by the linear relationship between TPD peak areas and 1-alkyne coverages (insets in Figure 4). This is in contrast with the behavior observed previously on reduced $\text{TiO}_2(001)$ on which the conversion of alkynes to the corresponding aromatic products has been reported in earlier studies [67-69].

Figure 4. Coverage dependent TPD spectra for (a) ethyne, (b) propyne, and (c) 1-butyne on $\text{TiO}_2(110)$. The assignment of TPD peaks from Ti_{5c} sites, O_b sites, and multilayers (M) is indicated in each panel. The red traces correspond to the saturation coverage of compressed 1-alkyne layers on Ti_{5c} rows (before the appearance of the TPD features from the O_b sites). The blue traces correspond to the coverages of uncompressed layers as represented by the saturation of TPD peaks from Ti_{5c} sites (not assigned for ethyne). The insets show the TPD area vs. 1-alkyne coverage, θ . The absolute coverages were determined using the calibrated beam fluxes, measured sticking coefficients, and the dose times and are referenced relative to the number of Ti_{5c} sites ($1 \text{ ML} \equiv 5.2 \times 10^{14} \text{ cm}^{-2}$).

3.3 Absolute Saturation Coverages on Ti_{5c} Rows

As discussed in Section 3.1, the absolute coverages for all of the hydrocarbons studied were determined using the calibrated beam fluxes [59], measured sticking coefficients, and the dose times and are referenced relative to the number of Ti_{5c} sites ($1 \text{ ML} \equiv 5.2 \times 10^{14} \text{ cm}^{-2}$). The resulting coverages, θ_{peak} and θ_{sat} , that correspond to the uncompressed layers on Ti_{5c} (coverages that saturate the TPD peaks on Ti_{5c} sites, blue spectra, Figures 2-4) and compressed layers on Ti_{5c} (maximum coverage before the appearance of the desorption peaks from O_b sites, red spectra, Figures 2-4), respectively, are summarized in Table 2. The lengths of the molecules are also listed in Table 2 to allow for comparison with the lattice spacing of the Ti_{5c} ions of 2.95 Å [4]. The lengths were estimated by determining the longest distance between the hydrogens of the end CH_x groups of each molecule and subsequently adding two hydrogen atom van der Waals radii of 1.20 Å [70].

Number of carbons, <i>N</i>	n-alkanes			1-alkenes			1-alkynes		
	θ_{sat} [ML]	θ_{peak} [ML]	Chain Length [Å]	θ_{sat} [ML]	θ_{peak} [ML]	Chain Length [Å]	θ_{sat} [ML]	θ_{peak} [ML]	Chain Length [Å]
1	0.71	0.61	4.24						
2	0.56	0.37	5.50	0.57	0.38	5.50	0.67	-	5.79
3	0.53	0.35	6.68	0.53	0.35	6.53	0.62	0.45	6.71
4	0.50	0.33	7.97	0.50	0.33	7.80	0.67	0.50	7.98

Table 2. The coverages, θ_{peak} and θ_{sat} , that correspond to the saturation of uncompressed layers (coverages that saturate the TPD peaks on Ti_{5c}, blue spectra, Figures 2-4) and compressed layers on Ti_{5c} (maximum coverages before the appearance of the desorption peaks from O_b sites, red spectra, Figures 2-4), respectively. The molecule lengths are estimated by determining the longest distance between the hydrogens of the end CH_x groups of each molecule plus two van der Waals H atom radii of 1.20 Å [70]. The length values can be compared with the Ti_{5c}-Ti_{5c} distance of 2.95 Å [4].

The comparison in Table 2 clearly shows that methane θ_{peak} and θ_{sat} coverages of 0.61 and 0.71 ML are significantly higher compared to the rest of n-alkanes studied. This is clearly a consequence of the smaller molecular size of 4.46 Å. Interestingly the θ_{peak} and θ_{sat} coverages are very similar, indicating that only a small coverage increase can be attained by compressing the layer. The closest possible packing determined from the methane molecular size yields the maximum coverage of 0.66 ML in agreement with the observed θ_{sat} . On average, these saturation coverages can be interpreted as having two methane molecules bound per every three Ti_{5c} sites.

For C₂ - C₄ n-alkanes and 1-alkenes, the θ_{peak} coverages are very similar (0.33-0.38 ML) and on average correspond to one molecule per three Ti_{5c} sites. While for C₃ and C₄ molecules this is expected based on their chain length, the result is somewhat surprising for ethane and ethene that have sizes that are slightly smaller than the two neighboring Ti_{5c}-Ti_{5c} distances. Therefore higher uncompressed saturation coverages of one molecule per two Ti_{5c} sites could be expected. The failure of simple size arguments becomes even more apparent for θ_{sat} coverages, where, as the chain length increases for C₂ to C₄ from 5.50 to 7.97 Å, only a slight θ_{sat} decrease from 0.57 to 0.50 ML is observed. The 1-butene θ_{sat} coverage is consistent with a recent study by Henderson who has determined the saturation coverage of both *cis*-butene and isobutene on Ti_{5c} sites to be 0.5 ML [71, 72]. While for C₂ and C₃ molecules, the θ_{sat} coverages are in reasonable agreement with what one would expect based on the molecular sizes (0.54 and 0.44-0.45 ML, respectively) for C₄ molecules, a substantial difference is observed. For example, for butane, θ_{sat} is 0.50 ML, while its size yields a significantly lower expected maximum coverage of 0.37 ML. We speculate, that this observed increase is possibly the result of (a) stacking butane molecules in an oriented way to maximize their surface density (e.g. parallel $\diagup \diagdown$ rather than antiparallel $\diagup \diagup$) or (b) changes in their conformation to accommodate higher coverages (e.g. $\diagdown \diagup$ / $\diagup \diagdown$). Indeed, a recent study from Weaver's group provides clear evidence that propane complexes on PdO(101) undergo a configurational change with increasing coverage [73]. Such configurational flexibility is certain to influence the maximum coverages that can be obtained, and provides further motivation for future theoretical studies.

Further comparisons can be made for small n-alkanes where absolute coverages were reported on Pt(111) and PdO(101) [15, 49, 52, 74]. For example, using molecular beam techniques in combination with a calibrated leak, Carlsson and Madix found that the saturation monolayer coverages of C₁ - C₄ n-alkanes on Pt(111) change only slightly with chain length. The absolute values of 0.237, 0.227, 0.205, and 0.20 ML (relative to Pt surface density, 1ML = $15.1 \times 10^{14} \text{ cm}^{-2}$) were determined for methane, ethane, propane, and n-butane [15]. On PdO(110), the ethane, propane, and n-butane coverages on Pd_{cus} sites were determined to be similar and equal to ~0.08 ML (relative to Pd atom density on Pd(111) surface, 1 ML = $15.3 \times 10^{14} \text{ cm}^{-2}$) [49, 52, 74].

To facilitate the coverage comparison on such different surfaces we use the saturation coverages and calculate the average molecule-molecule distances. On Ti_{5c} rows of TiO₂(110), a simple analysis yields molecule-molecule distances of 4.2, 5.3, 5.6 and 5.9 Å for compressed layers and 4.8, 8.0, 8.4, and 8.9 Å for uncompressed layers of methane, ethane, propane, and n-butane, respectively. These values can be compared with molecule-molecule separation in 3-dimensions using liquid densities of alkanes (assuming the face-centered close packing). This approach yields values of 4.5, 5.1, 5.6, and 6.1 Å for methane, ethane, propane, and n-butane in the liquid phase, respectively [75]. Clearly, the molecule-molecule distances in compressed layers on TiO₂(110) are not very different from those in the corresponding bulk liquids. For alkanes on Pt(111), where the molecules are arranged in a close-packed 2-dimensional layer, the average molecule-molecule distances obtained from the overlayer densities are 5.7, 5.8, 6.1, and 6.2 Å for methane, ethane, propane, and n-butane, respectively. On corrugated PdO(101), where Pd_{cus} binding sites are also arranged in rows, the reported molecule-molecule distances for ethane, propane, and n-butane bound on the Pd_{cus} rows are significantly larger, ~13 Å [49, 52, 74].

For 1-alkynes, the θ_{peak} coverages can be determined only for propyne and butyne and are equal to 0.45 and 0.50 ML, respectively. These values (one molecule per two Ti_{5c} sites) are higher than those for C₃ and C₄ n-alkanes and 1-alkenes (one molecule per three Ti_{5c} sites) despite their similar length. This can be further seen for θ_{sat} coverages of alkynes which are also higher: 0.62 - 0.67 ML or two molecules per three

Ti_{5c} sites rather than one molecule per two Ti_{5c} observed for C₂ – C₄ n-alkanes and 1-alkenes. Clearly, to better understand the coverage-dependent adsorption configurations of small hydrocarbons on TiO₂(110), future theoretical studies will be necessary.

3.4 Coverage Dependent Desorption Energies

We now continue with a more detailed analysis of the TPD spectra. To extract the kinetic parameters for desorption, we use a direct inversion of the Polanyi-Wigner equation [60, 63, 64]:

$$-\frac{d\theta}{dt} = \nu(\theta, T)\theta^n \exp\left(-\frac{E_d(\theta)}{RT}\right).$$

in which θ is the adsorbate coverage, t the time, ν the prefactor of desorption, n the desorption order, E_d the activation energy of desorption, R the gas constant, and T the temperature. T and t are related by $dT/dt = \beta$, where β is the heating rate. In the analysis, we assume first-order desorption kinetics ($n = 1$) and a coverage and temperature independent prefactor. The coverage dependent desorption energy is given by

$$E(\theta) = -RT \ln\left(-\frac{\beta}{\nu\theta} \frac{d\theta}{dT}\right).$$

The optimum value of ν can be determined by treating it as a variational parameter to minimize the difference between a set of simulated TPD spectra and corresponding experimental data [39, 43, 44]. This procedure has proven to work well when E_d varies weakly with θ [39, 43, 44]. However, for small hydrocarbons on TiO₂(110), particularly for 1-alkynes, E_d varies significantly with θ . Consequently, varying ν over a relatively broad range has little impact on the simulated TPD spectra. This has been shown previously for O₂, N₂, CO, and CO₂ on TiO₂(110) [62-64]. While we cannot determine the values of ν , we can bracket the range of their physically meaningful bounds using simple transition state theory models [39, 43, 44]. The value of ν for an elementary process such as molecular desorption can be calculated from the ratio of the partition function of the molecule in the transition state, $q^\ddagger$, to the partition function of the molecule in the initial state, q_{ads} as follows [76]:

$$\nu = \frac{k_B T}{h} \frac{q^\ddagger}{q_{ads}}.$$

Here, k_B is the Boltzmann constant and h the Planck's constant. The two bounds assume that at the transition state molecules have full freedom of rotational motion in 3-dimensions and translation motion in 2-dimensions.

The maximum, physically reasonable prefactor, ν_{max} , is calculated by considering the lower limit of the adsorbate partition function, q_{ads} . In this scenario the adsorbed molecules are considered to be fully hindered in all translational and rotational modes and $q_{ads} = 1$. The n-alkane length, N , dependent ν_{max} , subsequently follows as:

$$\nu_{max} = \alpha_{max} T^{3.5},$$

where α_{Max} is a constant that is a function of the moments of inertia of the molecule and of physical constants [39, 43, 44].

The second limit, the minimum, physically reasonable prefactor, ν_{min} , calculated by considering the case where the adsorbate partition function, q_{ads} is maximized. Here the degrees of freedom of the molecule in the adsorbed state are maximized by assuming a corrugation-free surface potential so that the adsorbate is able to rotate and translate freely in the plane of the surface and along its axis, but not out of plane. In this case, the initial state partition function is large and cancels most of the transition state partition function and ν_{min} can be expressed as:

$$\nu_{min} = \alpha_{min} T^x,$$

where $x = 1$ for $N = 1$, $x = 1.5$ for $N = 2$, and $x = 2$ for $N = 3-10$, and α_{min} is a constant that is a function of the moments of inertia of the molecule and of physical constants [39, 43, 44].

N	n-alkanes		1-alkenes		1-alkynes	
	ν_{max} [s ⁻¹]	$\overline{E_d}$ [kJ/mol]	ν_{max} [s ⁻¹]	$\overline{E_d}$ [kJ/mol]	ν_{max} [s ⁻¹]	$\overline{E_d}$ [kJ/mol]
1	7.9×10^{14}	25				
2	1.1×10^{17}	40	2.2×10^{17}	50	2.9×10^{17}	58
3	5.3×10^{18}	53	1.3×10^{19}	71	1.0×10^{19}	65
4	4.0×10^{19}	65	6.5×10^{19}	78	5.8×10^{19}	74

Table 3. The maximum, physically reasonable prefactors, ν_{max} , (calculated from the transition state theory) used in the inversion analysis in Figure 5, and the most probable desorption energies, $\overline{E_d}$, at the peaks of the distributions on Ti_{5c} sites in Figure 6.

We performed the inversion analysis using both ν_{min} and ν_{max} limits for T at the TPD peak maxima from Ti_{5c} sites. Due to the high topographic and electronic corrugation of potential energy surfaces on TiO₂(110), we expect that ν_{max} is a physically more reasonable approximation describing the desorption of hydrocarbons from the Ti_{5c} sites on TiO₂(110). Therefore in Figure 5, the results of the inversion analysis for n-alkanes (Figure 5a), 1-alkenes (Figure 5b) and 1-alkynes (Figure 5c) are shown using ν_{max} values (see Table 3). Analogous plots for ν_{min} are displayed in Figure S2 in SI.

Figure 5. Coverage dependent desorption energy, $E_d(\theta)$, for (a) n-alkanes, (b) 1-alkenes and (c) 1-alkynes on TiO₂(110). The desorption dependencies were obtained using the inversion analysis of the high coverage experimental TPD spectra shown in Figures 2 – 4. First order desorption and a constant, maximum physically reasonable prefactors, ν_{max} , (see Table 3) were used. The arrows

with Ti_{5c} and O_b symbols approximately indicate the plateau regions that correspond to the coverages where TPD peaks on Ti_{5c} and O_b sites develop. The blue and red circles correspond to the θ_{peak} and θ_{sat} coverages obtained from the TPD spectra in Figures 2 – 4.

The general line shape of the E_d vs. θ dependencies for all hydrocarbons is rather similar. At very low coverages (< 0.1 ML), a sharp decrease is observed for all studied hydrocarbons. This region likely corresponds to the coverage range where molecules are desorbing from the higher energy sites such as V_o 's despite that no distinct desorption features are observed in the TPDs. Note, that the small bump in the E_d vs. θ dependencies for n-alkanes in this coverage range is a result of an artifact (likely desorption from the sample holder as discussed above, see also Figure 2). At higher coverages, two relatively flat regions correspond to desorption from Ti_{5c} and O_b sites are observed (marked Ti_{5c} and O_b in Figure 5). The Ti_{5c} regions correspond to the coverages where the well-defined TPD peaks from the Ti_{5c} sites develops and increases in the intensity. The highest coverages, θ_{peak} , at which the peaks maximize (marked with blue circles, values summarized in Table 2) correspond to blue TPD spectra shown in Figures 2 - 4. Above θ_{peak} coverages, the energy starts to drop due to the development of the compression region where the molecules cannot adopt their most favorable configurations (discussed above). This compression continues until the saturation coverages, θ_{sat} , (see Table 2) are reached. These coverages are highlighted by red spectra in Figures 2 - 4 and marked by red circles in Figure 5.

Comparisons within each series (n-alkanes, 1-alkenes, and 1-alkynes) show that the E_d values increase with each additional CH_x segment by approximately the same amount, ΔE_d , that is different at different coverages (e.g. different increments on Ti_{5c} and O_b sites). The only significant deviation can be seen for 1-alkenes, where ΔE_d between ethene and propene is significantly larger than that between propene and 1-butene. The differences in desorption energies for different hydrocarbons adsorbed on different sites can be further visualized by plotting the distributions of their desorption energies, $P(E_d)$ as a function of E_d :

$$P(E_d) = -\frac{d\theta}{dE_d(\theta)}$$

The results of such distributions are plotted in Figure 6. Well-defined peaks corresponding to the most probable desorption energies, $\overline{E_d}$, from the O_b and Ti_{5c} sites and their increase with increasing chain length can be clearly seen. The values of E_d at the θ_{peak} and θ_{sat} coverages are also highlighted with blue and red circles, respectively.

Figure 6. The desorption energy distributions, $P(E_d)$, as a function of desorption energy E_d for (a) n-alkanes, (b) 1-alkenes and (c) 1-alkynes on $TiO_2(110)$. The most probable desorption energies, $\overline{E_d}$, for O_b and Ti_{5c} sites are marked as O_b and Ti_{5c} , respectively. The small peaks for n-alkanes in (a) marked with x are due to experimental artifact (see text for further discussion). The blue and red circles correspond to the θ_{peak} and θ_{sat} coverages obtained from the TPD spectra in Figures 2 – 4.

To further evaluate the E_d chain length dependencies for all the hydrocarbons we select two constant coverages of 0.1 and 0.4 ML and plot the obtained E_d values in Figure 7a and 7b, respectively. We select 0.1 ML as a low coverage limit where the adsorbate – adsorbate interactions on Ti_{5c} rows are minimized and the molecules bind in a most favorable way. This coverage is also above the coverage where the steep decrease of E_d vs. θ dependence is observed in Figure 5 and therefore should be relatively unaffected by desorption from defect sites. The coverage of 0.4 ML, on the other hand, is selected as a high coverage

limit that is close to the θ_{peak} coverages where the TPD peaks on Ti_{5c} sites maximize (blue traces in Figures 2 - 4).

Figure 7. Desorption energy vs chain length, N , for n-alkanes (squares), 1-alkenes (circles) and 1-alkynes (triangles) on $TiO_2(110)$. The desorption energies plotted here are taken from the dependencies shown in Figure 5 at (a) 0.1 ML and (b) 0.4 ML (b). The lines are linear regression fits to each data set.

We first focus on the dependencies observed for n-alkanes (squares, Figure 7a, b). At both coverages, a good linear relationship between the desorption energy and chain length is observed as demonstrated by the linear fits (black solid lines). This is in agreement with prior studies of alkanes on different metal and metal oxide surfaces [2, 20-23, 39, 44, 47, 74, 77]. Similar slopes of 14.6 and 12.2 kJ/mol/ N and the E_d axis intercepts of 17 and 14 kJ/mol are obtained at 0.1 and 0.4 ML, respectively. The slightly smaller value at 0.4 ML is likely a consequence of repulsive interactions or less favorable adsorption geometries due to higher coverage. The slope values, ΔE_d , represent the binding energy increase due to each additional CH_2 segment in C_NH_{2N+2} and can be compared with ΔE_d values reported on $MgO(100)$, graphene/Pt(111), Pt(111), and PdO(101) of 7.1, 8.5, 12.7, 16.5 kJ/mol, respectively [39, 44, 47, 74]. As one can see, the ΔE_d on Ti_{5c} sites of $TiO_2(110)$ is significantly larger than that on relatively weakly-binding substrates such as $MgO(100)$ and graphene but is comparable to more strongly-binding systems such as Pt(111) and PdO(101). The observed E_d axis intercept (17 and 14 kJ/mol for 0.1 and 0.4 ML,

respectively) is rather large as compared to the values of 3-7 kJ/mol observed previously on MgO(001), graphene/Pt(111), and Pt(111) [39, 44].

The offset for the highly active PdO(101), which efficiently oxidizes all alkanes except methane and ethane [47, 48], was found to be even higher, 25 kJ/mol [74, 77], and was attributed to the dative bonding interactions between the alkanes and the cus-Pd atoms of the PdO(101) surface [47, 50, 51, 74]. The alkane length independent enhancement suggested that the molecule-surface dative bonding produces a similar contribution to the total binding energy for all the *n*-alkanes (C₁ to C₅) studied. While the contribution of such dative bonding on TiO₂(110) is also possible, theoretical calculations are required to determine its extent. It is also possible that the high value arises from the large corrugation of the potential energy surface along the Ti_{5c} row which does not allow for the optimum binding of all CH_x segments. This can be illustrated by comparing the hypothetical binding of methane and ethane. While methane can maximize the van der Waals interactions with the Ti_{5c} site by being bound on top, ethane with the C-C distance of 1.5 Å, which is much shorter than the Ti_{5c} – Ti_{5c} distance of 2.95 Å, likely binds symmetrically with the same distance of both methyl groups from the Ti_{5c} site with a lower average binding energy per each segment. This effect propagates for longer chain *n*-alkanes, leading to the observed E_d offset.

Further comparisons can be carried out for C₂ hydrocarbons (*N* = 2), ethane, ethene and ethyne, each having two equivalent carbon atoms in sp³, sp² and sp hybridization, respectively, and only slight differences in their carbon - carbon bond lengths of 1.52, 1.34, and 1.21 Å. These molecules allow us to evaluate the changes in binding energies as a result of the presence of the C-C double and triple bonds. A significant increase is observed for ethene and even more so for ethyne relative to ethane. At 0.1 ML and 0.4 ML, the values increase to 58 and 47 kJ/mol for ethene and 64 and 52 kJ/mol for ethyne relative to 46 and 39 kJ/mol for ethane, respectively. This substantial increase is likely a result of the dative bonding from the π system of the molecules to the Ti⁴⁺ cations. A similar, but stronger dative bonding is well-

recognized on metal surfaces and generally plays an important role in alkene and alkyne activation in catalytic reactions [24-26, 29, 78].

Surprisingly, the E_d enhancement due to the presence of carbon-carbon double and triple bonds decreases with increasing chain length of 1-alkenes and 1-alkynes. This is clearly evident from the lower slopes of the fitting lines as compared to those for n-alkanes. The interpretation is that the longer chains destabilize the optimum bonding configurations for the carbon-carbon double and triple bonds that are available to ethene and ethyne. Possibly, both ethene and ethyne are bound on top of the Ti_{5c} site with C=C (or C≡C) bond perpendicular to the row direction. This configuration cannot be accessed by longer 1-alkenes and 1-alkynes due to the presence of the chain and along the row configurations of C=C (or C≡C) bond have to be adopted. Ultimately, detailed quantum chemical calculations that correctly treat Van der Waals dispersion interactions will be required to shed light on the trends observed in this experimental study.

4. Conclusions

The adsorption and desorption of small hydrocarbons (C_1 - C_4) on $TiO_2(110)$ surface has been studied by a combination of temperature programmed desorption (TPD) and molecular beam dosing. Our results show that the sticking coefficients for all the hydrocarbons studied are close to unity at the adsorption temperature of 60 K. The inversion analysis of the TPD spectra demonstrates that the desorption energies for n-alkanes, 1-alkenes, and 1-alkynes adsorbed on Ti_{5c} sites increase almost linearly with the chain length, as has been noted in previous studies of n-alkanes on both metal and metal oxide surfaces [2, 20-23, 39, 44, 47, 74, 77]. Generally, the desorption energies increase from n-alkanes to 1-alkenes and to 1-alkynes of the same length. Specifically, depending on the coverage, the desorption energies for ethyne and ethene are 33 - 39 % and 20 - 26% higher than that of ethane. This is likely a consequence of dative bonding of the alkyne and alkene π system to the undercoordinated Ti_{5c} sites. The difference between the desorption energies decreases as the hydrocarbon chain length is increased from C_2 to C_4 . This is likely

due to less favorable adsorption configurations that the C=C and C≡C can adopt due to presence of the side chains.

Using the flux-calibrated molecular beam and the saturation of the Ti_{5c}-related TPD features we have also determined the absolute saturation coverages for all the hydrocarbons studied. The highest saturation coverage of approximately two CH₄ molecules per three Ti_{5c} sites is observed for methane. The saturation coverages of C₂ - C₄ are lower but nearly independent of the chain length. For n-alkanes and 1-alkenes there is approximately one molecule per every two Ti_{5c} sites while for 1-alkynes the saturation coverages approached two molecules per three Ti_{5c} sites. This difference is rather puzzling, since the sizes of alkane and alkene molecules are approximately the same. Based on the saturation coverages of small hydrocarbons on Ti_{5c} sites, different adsorption configurations can be envisioned for 1-alkynes with respect to n-alkanes and 1-alkenes on TiO₂(110). These results provide an excellent data set for future theoretical calculations, as well as a baseline for future experimental studies on other well-defined metal oxide surfaces, such as RuO₂(110) which is isostructural equivalent to TiO₂(110), but has been predicted to be able to activate the C-H bonds of small hydrocarbons.[47]

ASSOCIATED CONTENT

Supporting Information. Control experiments supporting the high temperature tails in n-alkane TPD spectra being an artifact, the inversion analysis of the TPD spectra using the $\nu_{\min}$, and the resulting dependencies for desorption energies vs. coverage, desorption energy distributions vs. desorption energy, and the desorption energies vs chain length for all hydrocarbons studied. These materials are available free of charge via the Internet at <http://pubs.acs.org>.

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REFERENCES

- [1] M.A. Henderson, The interaction of water with solid surfaces: fundamental aspects revisited, *Surf. Sci. Rep.*, 46 (2002) 1-308.
- [2] J.F. Weaver, A.F. Carlsson, R.J. Madix, The adsorption and reaction of low molecular weight alkanes on metallic single crystal surfaces, *Surf. Sci. Rep.*, 50 (2003) 107-199.
- [3] U. Diebold, The surface science of titanium dioxide, *Surf. Sci. Rep.*, 48 (2003) 53-229.
- [4] Z. Dohnálek, I. Lyubinetsky, R. Rousseau, Thermally-driven processes on rutile $\text{TiO}_2(110)-(1 \times 1)$: A direct view at the atomic scale, *Prog. Surf. Sci.*, 85 (2010) 161-205.
- [5] M.A. Henderson, I. Lyubinetsky, Molecular-Level Insights into Photocatalysis from Scanning Probe Microscopy Studies on $\text{TiO}_2(110)$, *Chem. Rev.*, 113 (2013) 4428-4455.
- [6] C.L. Pang, R. Lindsay, G. Thornton, Structure of Clean and Adsorbate-Covered Single-Crystal Rutile TiO_2 Surfaces, *Chem. Rev.*, 113 (2013) 3887-3948.
- [7] L. Chen, Z. Li, R.S. Smith, B.D. Kay, Z. Dohnálek, Molecular Hydrogen Formation from Proximal Glycol Pairs on $\text{TiO}_2(110)$, *J. Am. Chem. Soc.*, 136 (2014) 5559-5562.
- [8] C.T. Campbell, J.R.V. Sellers, Enthalpies and Entropies of Adsorption on Well-Defined Oxide Surfaces: Experimental Measurements, *Chem. Rev.*, 113 (2013) 4106-4135.

- [9] J.J.H.B. Sattler, J. Ruiz-Martinez, E. Santillan-Jimenez, B.M. Weckhuysen, Catalytic Dehydrogenation of Light Alkanes on Metals and Metal Oxides, *Chem. Rev.*, 114 (2014) 10613-10653.
- [10] I.-T. Trots, T. Zimmermann, F. Schüth, Catalytic Reactions of Acetylene: A Feedstock for the Chemical Industry Revisited, *Chem. Rev.*, 114 (2013) 1761-1782.
- [11] G.M. Leuty, A. Abu-Nada, M. Tsige, Multilayer Adsorption of Methane and Chloromethane on the Molybdenum (100) Surface, *J. Phys. Chem. C*, 116 (2012) 14514-14525.
- [12] C.-L. Kao, R.J. Madix, The Adsorption Dynamics of Molecular Methane, Propane, and Neopentane on Pd(111): Theory and Experiment, *J. Phys. Chem. B*, 106 (2002) 8248-8257.
- [13] J.F. Weaver, M. Ikai, A. Carlsson, R.J. Madix, Molecular adsorption and growth of n-butane adlayers on Pt(111), *Surf. Sci.*, 470 (2001) 226-242.
- [14] A.R. Bishop, G.S. Girolami, R.G. Nuzzo, Structural Models and Thermal Desorption Energetics for Multilayer Assemblies of the n-Alkanes on Pt(111), *J. Phys. Chem. B*, 104 (2000) 754-763.
- [15] A.F. Carlsson, R.J. Madix, Alkane Trapping onto Structured Alkane Monolayers on Pt(111) at Low Temperature, *J. Phys. Chem. B*, 104 (2000) 12237-12249.
- [16] D.F. Johnson, W.H. Weinberg, Quantification of the selective activation of C-H bonds in short chain alkanes: The reactivity of ethane, propane, isobutane, n-butane, and neopentane on Ir(111), *J. Chem. Phys.*, 103 (1995) 5833-5847.
- [17] C.R. Arumainayagam, G.R. Schoofs, M.C. McMaster, R.J. Madix, Dynamics of molecular adsorption of ethane with platinum(111): a supersonic molecular beam study, *J. Phys. Chem.*, 95 (1991) 1041-1047.
- [18] P.D. Szuromi, J.R. Engstrom, W.H. Weinberg, The reaction of saturated and unsaturated hydrocarbons with the (110)-(1 $\times$ 2) and (111) surfaces of iridium, *J. Chem. Phys.*, 80 (1984) 508-517.
- [19] T.S. Wittrig, P.D. Szuromi, W.H. Weinberg, The interaction of ethane, propane, isobutane, and neopentane with the (110) surface of iridium, *J. Chem. Phys.*, 76 (1982) 3305-3315.

- [20] S.M. Wetterer, D.J. Lavrich, T. Cummings, S.L. Bernasek, G. Scoles, Energetics and Kinetics of the Physisorption of Hydrocarbons on Au(111), *J. Phys. Chem. B*, 102 (1998) 9266-9275.
- [21] A.V. Teplyakov, A.B. Gurevich, M.X. Yang, B.E. Bent, J.G. Chen, NEXAFS and TPD studies of molecular adsorption of hydrocarbons on Cu(100): segmental correlations with the heats of adsorption, *Surf. Sci.*, 396 (1998) 340-348.
- [22] J.L. Brand, M.V. Arena, A.A. Deckert, S.M. George, Surface diffusion of n-alkanes on Ru(001), *J. Chem. Phys.*, 92 (1990) 5136-5143.
- [23] B.A. Sexton, A.E. Hughes, A comparison of weak molecular adsorption of organic molecules on clean copper and platinum surfaces, *Surf. Sci.*, 140 (1984) 227-248.
- [24] H. Öberg, Y. Nestsarenka, A. Matsuda, J. Gladh, T. Hansson, L.G.M. Pettersson, H. Öström, Adsorption and Cyclotrimerization Kinetics of C₂H₂ at a Cu(110) Surface, *J. Phys. Chem. C*, 116 (2012) 9550-9560.
- [25] H. Öström, D. Nordlund, H. Ogasawara, K. Weiss, L. Triguero, L.G.M. Pettersson, A. Nilsson, Geometric structure and chemical bonding of acetylene adsorbed on Cu(110), *Surf. Sci.*, 565 (2004) 206-222.
- [26] H. Öström, A. Föhlisch, M. Nyberg, M. Weinelt, C. Heske, L.G.M. Pettersson, A. Nilsson, Ethylene on Cu(110) and Ni(110): electronic structure and bonding derived from X-ray spectroscopy and theory, *Surf. Sci.*, 559 (2004) 85-99.
- [27] L.P. Wang, W.T. Tysoe, R.M. Ormerod, R.M. Lambert, H. Hoffmann, F. Zaera, Determination of the bonding and orientation of ethylene on palladium(111) by near-edge x-ray absorption fine structure and photoelectron spectroscopy, *J. Phys. Chem.*, 94 (1990) 4236-4239.
- [28] E.M. Stuve, R.J. Madix, Bonding and dehydrogenation of ethylene on palladium metal. Vibrational spectra and temperature-programed reaction studies on palladium(100), *J. Phys. Chem.*, 89 (1985) 105-112.

- [29] G. Kyriakou, J. Kim, M.S. Tikhov, N. Macleod, R.M. Lambert, Acetylene Coupling on Cu(111): Formation of Butadiene, Benzene, and Cyclooctatetraene, *J. Phys. Chem. B*, 109 (2005) 10952-10956.
- [30] M. Bowker, C. Morgan, N. Perkins, R. Holroyd, E. Fourre, F. Grillo, A. MacDowall, Ethene Adsorption, Dehydrogenation and Reaction with Pd(110): Pd as a Carbon 'Sponge', *J. Phys. Chem. B*, 109 (2004) 2377-2386.
- [31] F. Zaera, D. Chrysostomou, Propylene on Pt(111), *Surf. Sci.*, 457 (2000) 89-108.
- [32] C.J. Baddeley, M. Tikhov, C. Hardacre, J.R. Lomas, R.M. Lambert, Ensemble Effects in the Coupling of Acetylene to Benzene on a Bimetallic Surface: A Study with Pd{111}/Au, *J. Phys. Chem.*, 100 (1996) 2189-2194.
- [33] F. Zaera, On the Mechanism for the Hydrogenation of Olefins on Transition-Metal Surfaces: The Chemistry of Ethylene on Pt(111), *Langmuir*, 12 (1996) 88-94.
- [34] C.J. Baddeley, R.M. Ormerod, A.W. Stephenson, R.M. Lambert, Surface Structure and Reactivity in the Cyclization of Acetylene to Benzene with Pd Overlayers and Pd/Au Surface Alloys on Au{111}, *J. Phys. Chem.*, 99 (1995) 5146-5151.
- [35] X.-C. Guo, R.J. Madix, Oxygen-Activated Combustion of Alkenes on the Pd(100) Surface, *J. Am Chem. Soc.*, 117 (1995) 5523-5530.
- [36] J.R. Lomas, C.J. Baddeley, M.S. Tikhov, R.M. Lambert, Ethyne Cyclization to Benzene over Cu(110), *Langmuir*, 11 (1995) 3048-3053.
- [37] C.H. Patterson, R.M. Lambert, Molecular mechanisms in the cyclotrimerization of acetylene to benzene on palladium (111), *J. Phys. Chem.*, 92 (1988) 1266-1270.
- [38] K.A. Davis, D.W. Goodman, Propene Adsorption on Clean and Oxygen-Covered Au(111) and Au(100) Surfaces, *J. Phys. Chem. B*, 104 (2000) 8557-8562.
- [39] S.L. Tait, Z. Dohnálek, C.T. Campbell, B.D. Kay, n-alkanes on Pt(111) and on C(0001)/Pt(111): Chain length dependence of kinetic desorption parameters, *J. Chem. Phys.*, 125 (2006) 234308.

- [40] R.M. Slayton, C.M. Aubuchon, T.L. Camis, A.R. Noble, N.J. Tro, Desorption Kinetics and Adlayer Sticking Model of n-Butane, n-Hexane, and n-Octane on $\text{Al}_2\text{O}_3(0001)$, *J. Phys. Chem.*, 99 (1995) 2151-2154.
- [41] P.N. Yaron, M.T.F. Telling, J.Z. Larese, Thermodynamic Investigation of n-Hexane Thin Films Adsorbed on Magnesium Oxide, *Langmuir*, 22 (2006) 7203-7207.
- [42] T. Arnold, R.E. Cook, J.Z. Larese, Thermodynamic Investigation of Thin Films of Ethane Adsorbed on Magnesium Oxide, *J. Phys. Chem. B*, 109 (2005) 8799-8805.
- [43] S.L. Tait, Z. Dohnálek, C.T. Campbell, B.D. Kay, n-alkanes on $\text{MgO}(100)$. I. Coverage-dependent desorption kinetics of n-butane, *J. Chem. Phys.*, 122 (2005) 164707.
- [44] S.L. Tait, Z. Dohnálek, C.T. Campbell, B.D. Kay, n-alkanes on $\text{MgO}(100)$. II. Chain length dependence of kinetic desorption parameters for small n-alkanes, *J. Chem. Phys.*, 122 (2005) 164708.
- [45] R.E. Cook, T. Arnold, N. Strange, M. Telling, J.Z. Larese, Pentane Adsorbed on $\text{MgO}(100)$ Surfaces: A Thermodynamic, Neutron, and Modeling Study, *J. Phys. Chem. C*, 119 (2014) 332-339.
- [46] D. Fernández-Cañoto, J.Z. Larese, Thermodynamic and Modeling Study of Thin n-Heptane Films Adsorbed on Magnesium Oxide (100) Surfaces, *J. Phys. Chem. C*, 118 (2014) 3451-3458.
- [47] J.F. Weaver, C. Hakanoglu, A. Antony, A. Asthagiri, Alkane activation on crystalline metal oxide surfaces, *Chem. Soc. Rev.*, 43 (2014) 7536-7547.
- [48] A. Antony, A. Asthagiri, J.F. Weaver, Pathways and kinetics of methane and ethane C-H bond cleavage on $\text{PdO}(101)$, *J. Chem. Phys.*, 139 (2013) 104702.
- [49] C. Hakanoglu, F. Zhang, A. Antony, A. Asthagiri, J.F. Weaver, Selectivity in the initial C-H bond cleavage of n-butane on $\text{PdO}(101)$, *Phys. Chem. Chem. Phys.*, 15 (2013) 12075-12087.
- [50] A. Antony, A. Asthagiri, J.F. Weaver, Pathways for C-H bond cleavage of propane $[\sigma]$ -complexes on $\text{PdO}(101)$, *Phys. Chem. Chem. Phys.*, 14 (2012) 12202-12212.

- [51] J.F. Weaver, C. Hakanoglu, A. Antony, A. Asthagiri, High Selectivity for Primary C–H Bond Cleavage of Propane σ -Complexes on the PdO(101) Surface, *J. Am. Chem. Soc.*, 133 (2011) 16196-16200.
- [52] J.F. Weaver, S.P. Devarajan, C. Hakanoglu, Facile C–H Bond Cleavage and Deep Oxidation of Propane on a PdO(101) Thin Film, *J. Phys. Chem. C*, 113 (2009) 9773-9782.
- [53] M. Rössler, S. Günther, J. Wintterlin, Scanning Tunneling Microscopy of the RuO₂(110) Surface at Ambient Oxygen Pressure, *J. Phys. Chem. C*, 111 (2007) 2242-2250.
- [54] U.A. Paulus, Y. Wang, H.P. Bonzel, K. Jacobi, G. Ertl, Adsorption of ethylene on stoichiometric RuO₂(1 1 0), *Surf. Sci.*, 566–568 (2004) 989-994.
- [55] L. Chen, Z.J. Li, R.S. Smith, B.D. Kay, Z. Dohnalek, Conversion of 1,2-Propylene Glycol on Rutile TiO₂(110), *J. Phys. Chem. C*, 118 (2014) 15339-15347.
- [56] L. Chen, Z. Li, R.S. Smith, B.D. Kay, Z. Dohnálek, Conversion of 1,3-Propylene Glycol on Rutile TiO₂(110), *J. Phys. Chem. C*, 118 (2014) 23181-23188.
- [57] M.A. Henderson, Structural Sensitivity in the Dissociation of Water on TiO₂ Single-Crystal Surfaces, *Langmuir*, 12 (1996) 5093-5098.
- [58] D.A. King, M.G. Wells, Molecular beam investigation of adsorption kinetics on bulk metal targets: Nitrogen on tungsten, *Surf. Sci.*, 29 (1972) 454-482.
- [59] Z. Li, R.S. Smith, B.D. Kay, Z. Dohnálek, Determination of Absolute Coverages for Small Aliphatic Alcohols on TiO₂(110), *J. Phys. Chem. C*, 115 (2011) 22534-22539.
- [60] Z. Dohnálek, G.A. Kimmel, S.A. Joyce, P. Ayotte, R.S. Smith, B.D. Kay, Physisorption of CO on the MgO(100) Surface, *J. Phys. Chem. B*, 105 (2001) 3747-3751.
- [61] Z. Dohnálek, R.S. Smith, B.D. Kay, Adsorption Dynamics and Desorption Kinetics of Argon and Methane on MgO(100), *J. Phys. Chem. B*, 106 (2002) 8360-8366.

- [62] X. Lin, Y. Yoon, N.G. Petrik, Z. Li, Z.-T. Wang, V.-A. Glezakou, B.D. Kay, I. Lyubinetsky, G.A. Kimmel, R. Rousseau, Z. Dohnálek, Structure and Dynamics of CO₂ on Rutile TiO₂(110)-1×1, *J. Phys. Chem. C*, 116 (2012) 26322-26334.
- [63] Z. Dohnálek, J. Kim, O. Bondarchuk, J.M. White, B.D. Kay, Physisorption of N₂, O₂, and CO on Fully Oxidized TiO₂(110), *J. Phys. Chem. B*, 110 (2006) 6229-6235.
- [64] R.S. Smith, Z. Li, L. Chen, Z. Dohnálek, B.D. Kay, Adsorption, Desorption, and Displacement Kinetics of H₂O and CO₂ on TiO₂(110), *J. Phys. Chem. B*, 118 (2014) 8054-8061.
- [65] G.A. Kimmel, M. Persson, Z. Dohnálek, B.D. Kay, Temperature independent physisorption kinetics and adsorbate layer compression for Ar adsorbed on Pt(111), *J. Chem. Phys.*, 119 (2003) 6776-6783.
- [66] J.S. Chickos, W.E. Acree, Enthalpies of Sublimation of Organic and Organometallic Compounds. 1910–2001, *J. Phys. Chem. Ref. Data*, 31 (2002) 537-698.
- [67] A.B. Sherrill, V.S. Lusvardi, M.A. Barteau, Investigation of Cyclooctatetraene on Reduced TiO₂(001) as a Possible Intermediate in Alkyne Cyclotrimerization, *Langmuir*, 15 (1999) 7615-7620.
- [68] K.G. Pierce, M.A. Barteau, Cyclotrimerization of Alkynes on Reduced TiO₂(001) Surfaces, *J. Phys. Chem.*, 98 (1994) 3882-3892.
- [69] K.G. Pierce, M.A. Barteau, Cyclotrimerization of sterically hindered alkynes in ultrahigh vacuum: TPD of tert-butylacetylene on the reduced TiO₂(001) surface, *Surf. Sci.*, 326 (1995) L473-L476.
- [70] S.S. Batsanov, Van der Waals Radii of Elements, *Inorg. Mater.*, 37 (2001) 871-885.
- [71] M.A. Henderson, Comparison of the Photodesorption Activities of cis-Butene, trans-Butene, and Isobutene on the Rutile TiO₂(110) Surface, *J. Phys. Chem. C*, 117 (2013) 23840-23847.
- [72] M.A. Henderson, Photooxidation and Photodesorption in the Photochemistry of Isobutene on TiO₂(110), *J. Phys. Chem. C*, 117 (2013) 14113-14124.

- [73] F. Zhang, L. Pan, J. Choi, V. Mehar, J.T. Diulus, A. Asthagiri, J.F. Weaver, Propane σ -Complexes on PdO(101): Spectroscopic Evidence of the Selective Coordination and Activation of Primary C-H Bonds, *Angew. Chem. Int. Ed.*, DOI: 10.1002/anie.201505237.
- [74] J.F. Weaver, C. Hakanoglu, J.M. Hawkins, A. Asthagiri, Molecular adsorption of small alkanes on a PdO(101) thin film: Evidence of σ -complex formation, *J. Chem. Phys.*, 132 (2010) 024709.
- [75] <http://encyclopedia.airliquide.com>.
- [76] D.A. McQuarrie, *Statistical Mechanics*, Harper & Row, New York, , 1976.
- [77] A. Antony, C. Hakanoglu, A. Asthagiri, J.F. Weaver, Dispersion-corrected density functional theory calculations of the molecular binding of n-alkanes on Pd(111) and PdO(101), *J. Chem. Phys.*, 136 (2012) 054702.
- [78] Y. Sohn, W. Wei, J.M. White, Phenylacetylene on Cu(111): Adsorption Geometry, Interfacial Electronic Structures and Thermal Chemistry, *J. Phys. Chem. C*, 111 (2007) 5101-5110.