Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Adsorption of Alkanes on Stoichiometric and Oxygen-Rich $RuO_2(110)$

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Surface structure of stoichiometric and O-rich $RuO_2(110)$

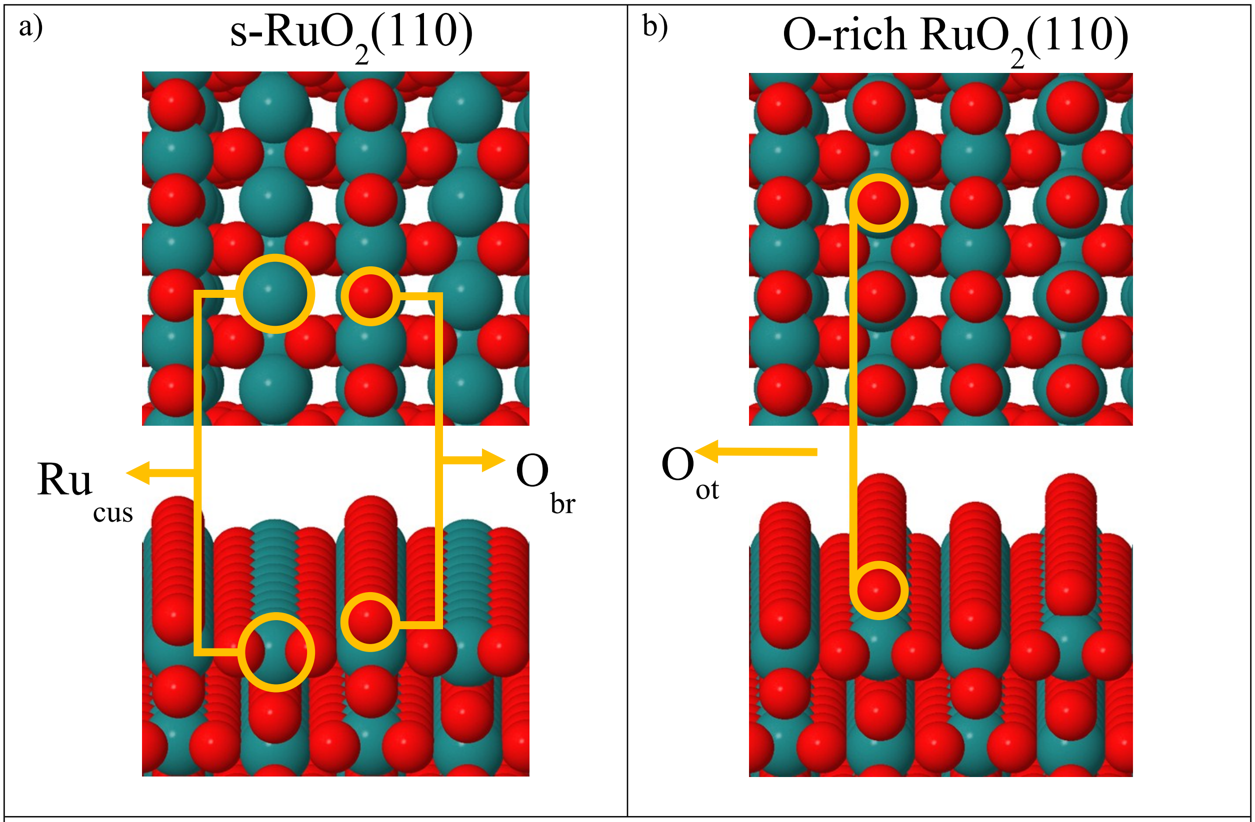


Figure S1: Top and isometric views of the a) stoichiometric and b) O-rich $RuO_2(110)$ surfaces with Ru_{cus}, O_{br} and O_{ot} atoms labeled.

Figure S1 shows model representations of the $RuO_2(110)$ surface with stoichiometric and O-rich terminations where the Ru_{cus}, O_{br} and O_{ot} atoms are labeled. The image of the O-rich surface shows a 100% coverage of O_{ot} atoms, but the O_{ot} coverage can be varied as discussed below.

Generation of on-top oxygen atoms on $RuO_2(110)$

Figure S2 shows O_2 TPD spectra obtained from O_{ot}-covered $RuO_2(110)$. We prepared different coverages of on-top oxygen (~4% to 86%) on $RuO_2(110)$ by performing a saturation exposure of O_2 (green, bold) at a surface temperature of 300 K, followed by flashing to various temperatures (T_{flash}) to desorb targeted amounts of O_{ot} atoms from the Ru_{cus} rows. We prepared a surface with 96% O_{ot} atoms by doing ~60 L O_2 while lowering the surface temperature from 500 K to 300 K at a rate of 10 K/min.[1]

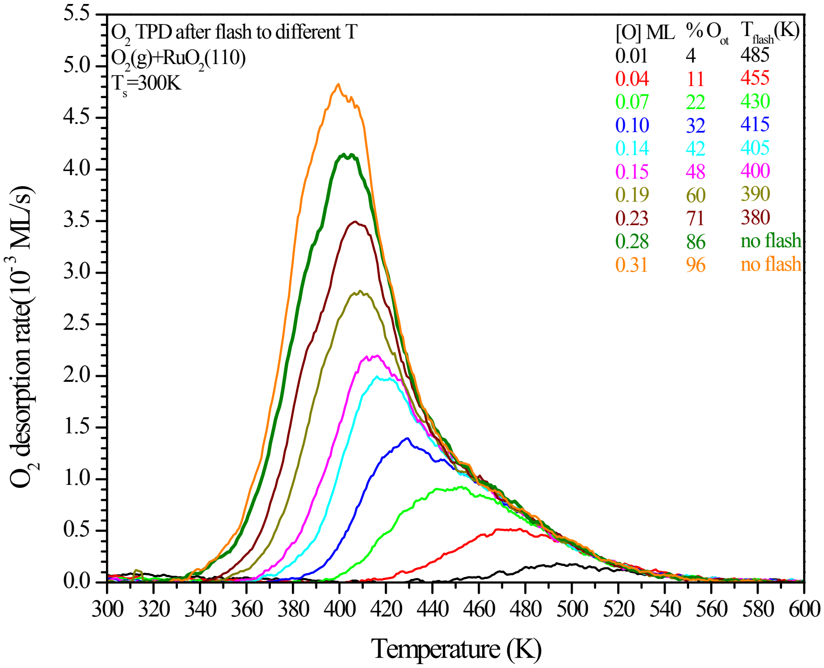


Figure S2. O_2 TPD spectra obtained from different O_{ot} atom coverages on $RuO_2(110)$ prepared by a saturation exposure of O_2 (green, bold) at 300 K, followed by flashing to different temperature to desorb a fraction of the on-top oxygen. A surface with 96% O_{ot} coverage was prepared by exposing $RuO_2(110)$ to 60 L O_2 while decreasing the surface temperature from 500 K to 300 K (10 K/min).

Alkane adsorption on Ru(0001)

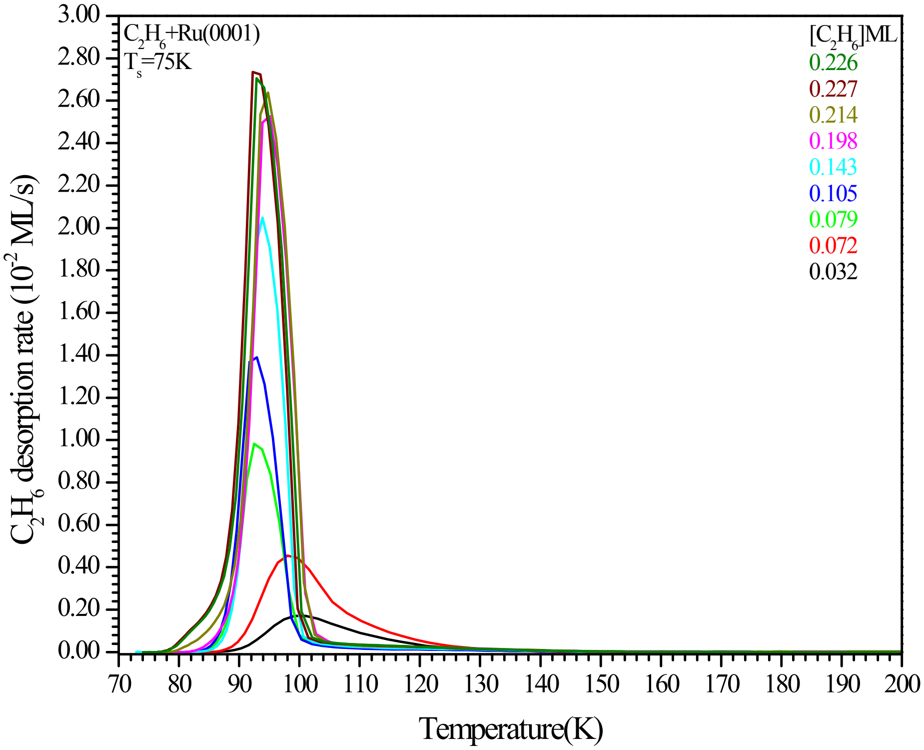
Figure S3a shows ethane TPD spectra obtained after generating various coverages of ethane on Ru(0001) at 75 K. At low coverage, ethane molecules initially physisorb on Ru(0001) and desorb in a peak centered at ~100 K. This peak gradually shifts to lower temperature until reaching

~94 K at high coverage. Desorption from the multilayer gives rise to the smaller peak at about 82 K and begins to occur at total coverages above 0.227 ML.[2]

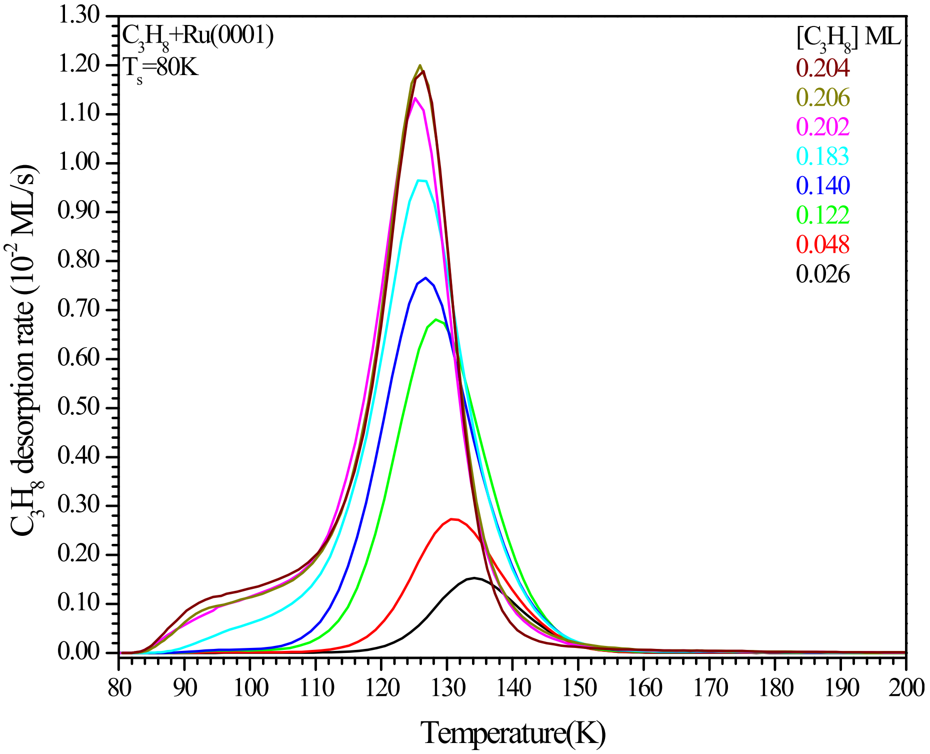
Figure S3b shows a series of propane TPD spectra obtained after generating various coverages of propane on Ru(0001) at 80 K. At low coverage, the propane desorption peak centers at ~134 K, which is consistent with physisorbed propane on the metal surface. This feature shifts to lower desorption temperature with increasing propane coverage and saturates at about 0.205 ML[2] with the desorption peak centered at ~126 K. The broad feature at about 93 K is consistent with second layer desorption of propane from the metal surface.

Figure S3c shows a series of n-butane TPD spectra obtained after generating various n-butane coverages on Ru(0001) at 85 K. At low coverage, n-butane initially desorbs in a single peak centered at about 156 K. As its coverage surpasses about 0.1 ML, distinct features centered at 102 K and 117 K appear, which agrees well with a previous study.[3] Weaver et al. have shown that at n-butane coverages below 0.14 ML, a disordered monolayer forms in which the n-butane molecules lie parallel to the surface to minimize their binding energy. At coverage between 0.14 ML to 0.20 ML, butane molecules develop into an ordered arrangement within the monolayer and lie parallel to the surface. Above 0.20 ML, a more densely-packed, ordered n-butane phase forms at lower temperature.

(a)


C_2H_6+Ru(0001)
T_s=75K
[C_2H_6]ML
0.226
0.227
0.214
0.198
0.143
0.105
0.079
0.072
0.032
C_2H_6 desorption rate (10^{-2} ML/s)
3.00
2.80
2.60
2.40
2.20
2.00
1.80
1.60
1.40
1.20
1.00
0.80
0.60
0.40
0.20
0.00
70
80
90
100
110
120
130
140
150
160
170
180
190
200
Temperature(K)

(b)


C_3H_8+Ru(0001)
T_s=80K
[C_3H_8] ML
0.204
0.206
0.202
0.183
0.140
0.122
0.048
0.026
C_3H_8 desorption rate (10^{-2} ML/s)
1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
80
90
100
110
120
130
140
150
160
170
180
190
200
Temperature(K)

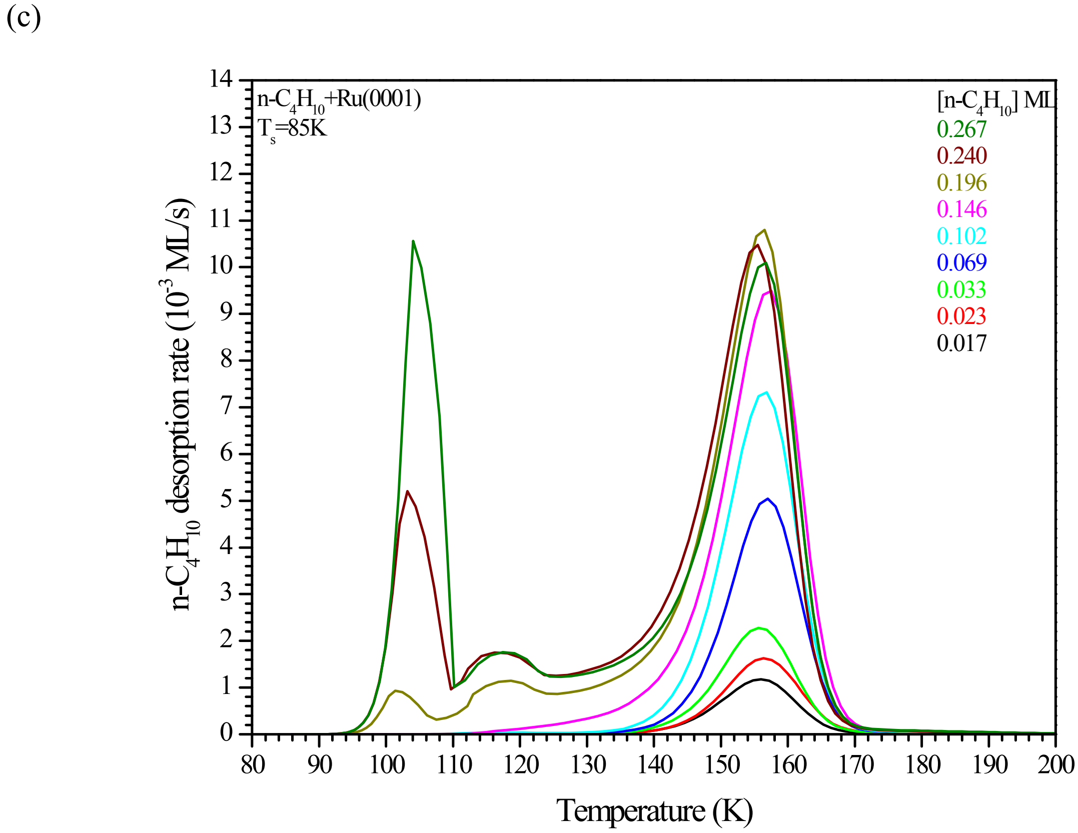


Figure S3. TPD spectra of (a) ethane, (b) propane, (c) n-butane obtained after generating various alkane coverages at 75 K (a), 80 K (b) and 85 K (c) on Ru(0001). The initial alkane coverages are listed in each figure.

Comparison of TPD peak temperatures of alkanes on Ru(0001) and s-RuO_2(110)

Following the work of Chen et al,[4] we list the TPD peak temperatures for the C_1 to C_4 alkanes adsorbed on Ru(0001) and s-RuO_2(110) at monolayer saturation in Table 1, and find that each peak temperature increases linearly as a function of the alkane chain length N. This linear increase is due in large part to an increase in the strength of the molecule-surface dispersion interaction with increasing alkane size. Similar behavior has been reported previously for alkanes adsorbed on several solid surfaces.[5-6] For s-RuO_2(110), the differential shift in peak temperature as a function of N is largest for the strongly-bound α state (42 K/N) and decreases to values of 30, 25 and 19 K/N for the β, γ_1 and γ_2 peaks, respectively. This trend shows that the contribution of each

CH_x group increases with the binding strength of the adsorbed state. Stronger dispersion interactions of alkanes with the Ru_{cus} sites compared with O_{br} sites are at least partly responsible for the larger differential shifts of the α and β states with increasing N compared with the γ_1 and γ_2 states. Dative bonding interactions between CH_x groups and the Ru_{cus} sites may also cause the differential shift of the α state to be larger than the shifts observed for the more weakly-bound alkane states on $RuO_2(110)$. The table also shows that the TPD peak temperatures for alkanes adsorbed in the α state on $RuO_2(110)$ are significantly larger than those for alkanes physically adsorbed on Ru(0001), and that the differential shift is also larger for the alkane α state on $RuO_2(110)$ than that for alkanes on Ru(0001) (42 vs. 28 K/N). As discussed in the manuscript, we find that formation of alkane σ-complexes on the Ru_{cus} sites enhances the binding of alkanes on $RuO_2(110)$ compared with alkanes that are physically adsorbed on Ru(0001).

Lastly, our results reveal that the TPD peak temperatures for the α state are higher than those reported by Chen et al.[4] for alkanes adsorbed on Ti_{cus} sites of $TiO_2(110)$, demonstrating much stronger dative bonding of alkanes on $RuO_2(110)$ compared with $TiO_2(110)$. In contrast, we find that the peak temperatures reported for alkanes adsorbed on O_{br} sites of $TiO_2(110)$ are nearly identical with the γ_2 peak temperatures that we observe for alkanes on $RuO_2(110)$, though they are slightly lower than the γ_1 peak temperatures. This comparison suggests that the alkane-O_{br} interaction strength is similar for $TiO_2(110)$ and $RuO_2(110)$. The stronger binding in the γ_1 vs. γ_2 state may indicate that a fraction of the alkanes on the O_{br} sites also interact with Ru_{cus} atoms and experience enhancing binding as a result.

Table S1. TPD peak temperatures for alkanes on Ru(0001) and s-RuO_2(110) at the alkane saturation coverages. Temperatures in parentheses were extrapolated from a linear fit to the peak temperature for the C_2 to C_4 alkanes for which we find $R^2 = 0.99$. Values in parentheses are extrapolated from the linear fits.

C_NH_{2N+2}	TPD peak temperature (K)				
N	Ru(0001)	s-RuO_2(110)			
		α	β	γ_1	γ_2
1	(74)	117	88	(67)	(68)
2	100	173	119	92	87
3	134	209	140	115	105
4	156	244	180	141	124
Desorption temperature differential shift (K/*N*)	28	42	30	25	19

Desorption pre-factors for alkanes on Ru(0001) and RuO_2(110)

To estimate desorption pre-factors, we use formulas for the minimum and maximum pre-factors that are based on transition state theory models,[6] where the transition state for desorption is taken as the gas-phase alkane molecule minus one translational degree of freedom. The desorption pre-factor is given by the following equation,

$$\nu_d = \frac{kT}{h}\frac{q_t^{2D} q_r q_v}{q_{ad}}$$

where q_t^{2D} is the partition function for alkane translation in two-dimensions, q_r is the partition function for alkane rotation in three dimensions, q_v is the vibrational partition function of the gas-phase alkane molecule and q_{ad} is the partition function for the adsorbed alkane. A maximum value of the desorption pre-factor (ν_{max}) is computed by assuming that the adsorbed alkane molecules are fixed at their binding sites (2D lattice gas), such that $q_{ad} = 1$, and that all vibrational partition functions of the alkane molecule are equal to unity.[6]

From the models, a minimum value of the desorption pre-factor (ν_{min}) is obtained by assuming that the adsorbed alkane molecule executes free motion in the surface plane (2D gas) and that all vibrational modes are in the ground state and thereby yield partition functions equal to unity. In this case, the partition function for the adsorbed alkane is approximated as $q_{ad} = q_t^{2D} q_r^{1D}$ since the three in-plane modes of the 2D gas are treated as two free translations and one free rotation, while the remaining modes are treated as frozen vibrations. It is worth mentioning that the minimum pre-factor computed using this approach may not represent the lowest value that is physically reasonable. In addition to the three free, in-plane motions, a 2D gas molecule also possesses three low-frequency, frustrated motions that are likely to populate excited states at temperatures where desorption occurs at appreciable rates. In such a case, the partition functions for these motions would exceed unity and thereby cause the pre-factor to decrease below the ν_{min} value determined by the model of Tait et al.[6] Formulas for the minimum and maximum pre-factors obtained from these models depend only on the molecular mass and moment of inertia of the alkane molecule as well as the temperature and are easily computed.

Table S2. Desorption pre-factors used in the Redhead analysis of the alkane TPD spectra. The pre-factors for alkane desorption from Ru(0001) were computed using the CS correlation[7] and the minimum and maximum values of the pre-factors were computed for the α TPD peaks of alkanes on s-RuO$_2$(110) using models reported by Tait et al.[6] A recent investigation provides evidence that the maximum desorption pre-factors accurately represent the actual desorption pre-factors for alkane complexes on RuO$_2$(110).[8]

Chain length	log$_{10}$(prefactor(s^{-1}))		
C_NH_{2N+2}	Ru(0001)	s-RuO$_2$(110)	
N		min	max
1	12.2	12.4	15.4
2	13.6	13.7	17.7
3	14.8	15.0	19.4
4	15.4	15.4	20.2

Table 2 shows the values of the minimum and maximum desorption pre-factors that we computed for each alkane at the α peak temperatures as well as the pre-factors determined using the CS correlation. We note that the CS correlation predicts desorption pre-factors that are intermediate to the ν_{min} and ν_{max} values, though closer to ν_{min}. The ν_{min} and ν_{max} values for alkane complexes on $RuO_2(110)$ span a range of three orders of magnitude for CH_4, with this range increasing to nearly five orders of magnitude for n-butane. Even though the limiting pre-factors span a wide range, recent results indicate that the ν_{max} values represent accurate estimates of the actual desorption pre-factors and can thus provide accurate estimates of the alkane binding energies on $RuO_2(110)$ from TPD analysis.[8]

Random sequential adsorption of dimers on a line of sites

We used a well-known model of the random sequential adsorption (RSA) of dimers on a line of sites to estimate how the occurrence probabilities of vacant Ru_{cus} k-mers as well as stranded Ru_{cus} sites could evolve with the O_{ot} coverage on $RuO_2(110)$.[9] The model shows that the probability for finding a vacant k-mer, which could be part of a larger series of vacant sites, is given by the formula,

$$P_k = P_1 e^{-(k-1)z} \quad (1)$$

where z is a dimensionless time and P_1 is the probability of finding a single vacant site. The probability P_1 is equal to $1 - \theta$, where θ is the fractional coverage of occupied sites (by O_{ot} atoms in the present case). Integration of the rate equation in the RSA model gives the following equation for P_1 as function of time,

$$P_1 = exp(2e^{-z} - 2) \quad (2)$$

Equation (1) may then be written to give P_k as a function of P_1 as follows,

$$P_k = P_1\left(\frac{1}{2}lnP_1 + 1\right)^{k-1} \quad (3)$$

From the definition of P_k, we recognize that P_1 is the probability of finding a single vacant site, irrespective of the occupancy of its neighboring sites, and thus includes vacant monomers, dimers, trimers, etc. Thus, the probability of finding a single vacant site with occupied nearest neighbor sites, a so-called "stranded" site, is equal to

$$P_{1,only} = P_1 - P_2 = \frac{1}{2} P_1 ln P_1 \qquad (4).$$

It is straightforward to show that the maximum value of $P_{1,only}$ occurs at $P_1 = e^{-1}$ or $\theta = 0.63$, which is close to the range of O_{ot} coverage (~40 to 60%) where we observe the maximum yield of C_2 to C_4 alkanes desorbing in the β TPD region.

References

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