Supporting Information for:

Theoretical Insight into Catalytic Propane Dehydrogenation on Ni(111)

Tinnakorn Saelee,[†] Supawadee Namuangruk,[§] Nawee Kungwan,*[,†,‡] and Anchalee Junkaew*[,§]

[†]*Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai, 50200, Thailand*

[‡]*Center of Excellence in Materials Science and Technology, Chiang Mai University, Chiang Mai 50200, Thailand*

[§]*National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA), Pathum Thani 12120, Thailand*

**Corresponding author e-mails: naweekung@gmail.com (N.K), anchalee@nanotec.or.th (A.J.)*

1. Propane and propylene adsorption on Ni(111)

Optimized possible structures of propane and propylene adsorption on Ni(111). An asterisk (*) denotes the most stable adsorbed structure of each adsorbate.

Table S1. All possible configurations of propane adsorption on Ni(111) and E_{ads} in eV

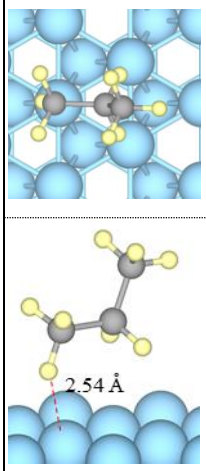
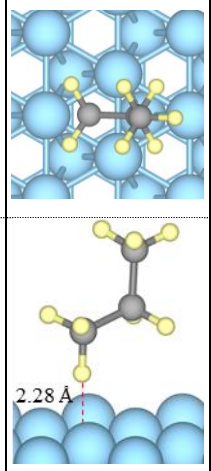
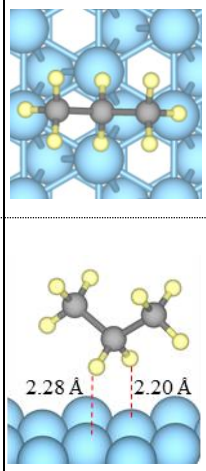
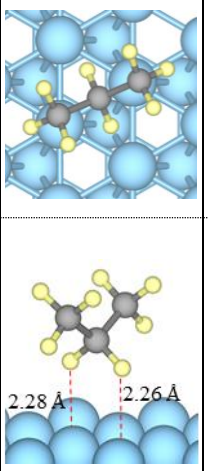
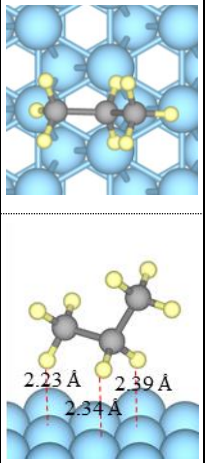
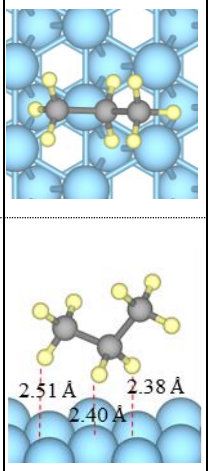
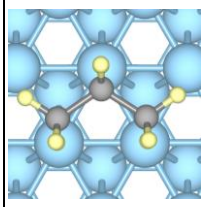
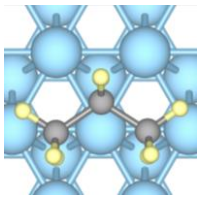
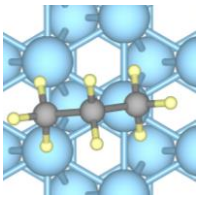
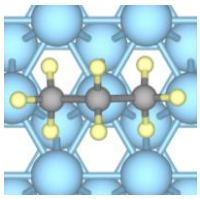
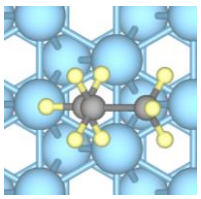
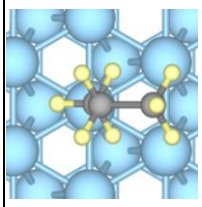
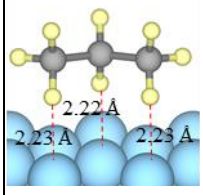
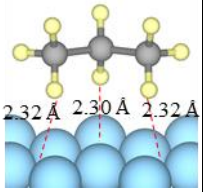
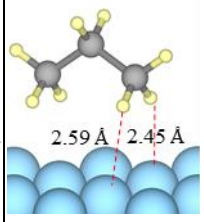
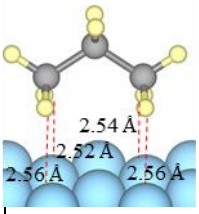
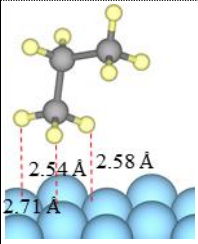
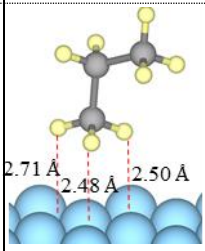
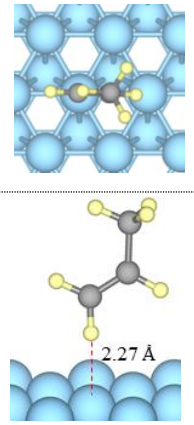
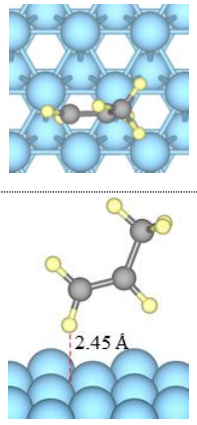
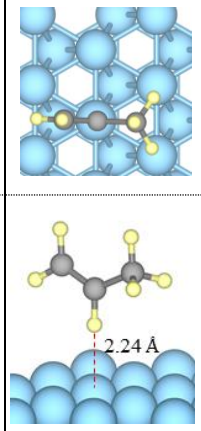
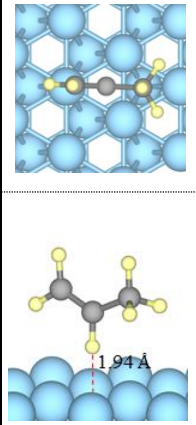
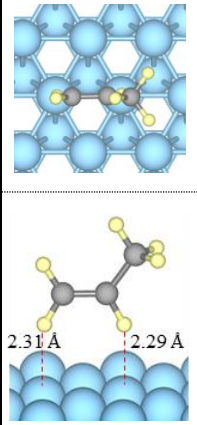
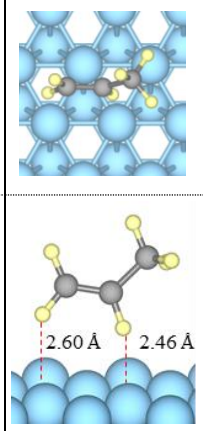
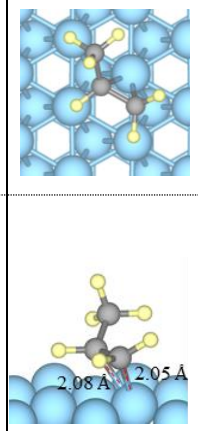
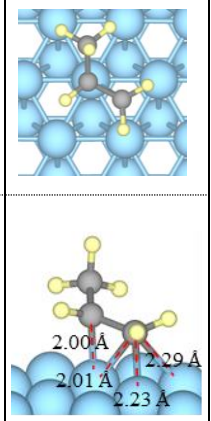
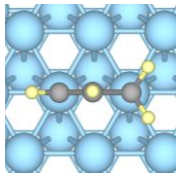
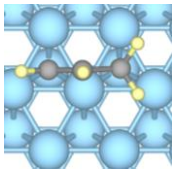
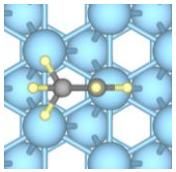
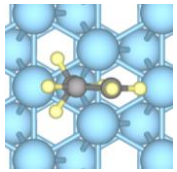
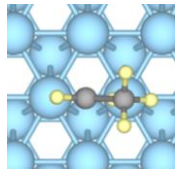
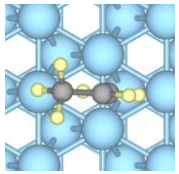
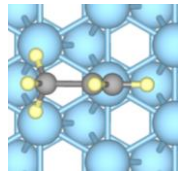
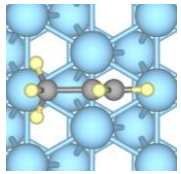
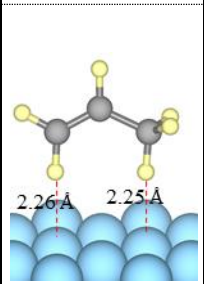
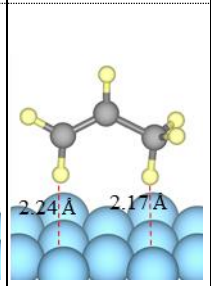
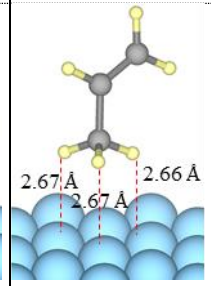
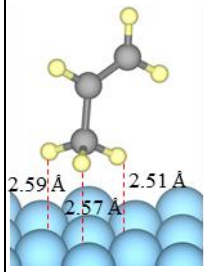
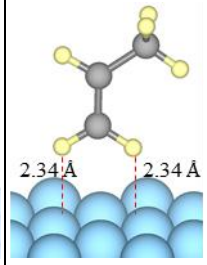
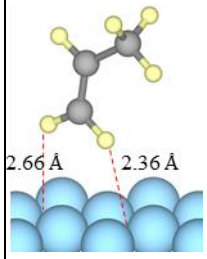
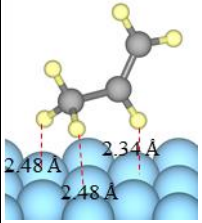
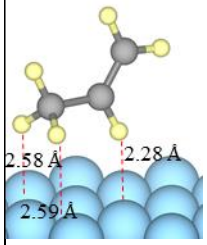
Propane1	Propane2	Propane3	Propane4	Propane5	Propane6
					
E_{ads} = -0.47	E_{ads} = -0.38	E_{ads} = -0.51	E_{ads} = -0.47	E_{ads} = -0.50	E_{ads} = -0.48
Propane7	Propane8	Propane9	Propane10	Propane11	Propane12
					
					
E_{ads} = **-0.61***	E_{ads} = -0.57	E_{ads} = -0.54	E_{ads} = -0.51	E_{ads} = -0.38	E_{ads} = -0.36

Table S2. All possible configurations of propylene adsorption on Ni(111) and E_{ads} in eV

Propylene1	Propylene2	Propylene3	Propylene4	Propylene5	Propylene6	Propylene7	Propylene8
							
E_{ads} = -0.31	E_{ads} = -0.38	E_{ads} = -0.41	E_{ads} = -0.40	E_{ads} = -0.41	E_{ads} = -0.44	E_{ads} = -1.15	**E_{ads} = -1.39***
Propylene9	Propylene10	Propylene11	Propylene12	Propylene13	Propylene14	Propylene15	Propylene16
							
							
E_{ads} = -0.44	E_{ads} = -0.43	E_{ads} = -0.35	E_{ads} = -0.34	E_{ads} = -0.27	E_{ads} = -0.30	E_{ads} = -0.43	E_{ads} = -0.44

2. Electronic charge analysis

Table S3. Bader charge analysis of selected atoms of Ni(111), propane and propylene before and during adsorption represented in Figure 2

Bader Charge change (|*e*|)						
System	**Ni(111)**		**Adsorbed molecules**			
			Propane		**Propylene**	
Isolated phase	Total	(0.000)	Total	(0.000)	Total	(0.000)
	Subsurface layer	(-0.084)	C^1	(+0.178)		
	Top layer	(-0.060)	C^2	(-0.221)		
			C^3	(+0.162)		
	Ni^1	(-0.026)	H^1	(-0.048)		
	Ni^2	(+0.046)	H^2	(-0.047)		
	Ni^3	(-0.150)	H^3	(-0.039)		
	Ni^1	(-0.057)			C^1	(-0.109)
	Ni^2	(-0.041)			C^2	(-0.102)
	Ni^3	(+0.046)			C^3	(-0.192)
					H^1	(+0.134)
					H^2	(-0.042)
Propane adsorption	Total	(-0.264)	Total	(+0.264)		
	Subsurface layer	(-0.027)	C^1	(-0.097)		
	Top layer	(-0.236)	C^2	(-0.206)		
			C^3	(-0.161)		
	Ni^1	(+0.129)	H^1	(+0.272)		
	Ni^2	(+0.316)	H^2	(+0.202)		
	Ni^3	(+0.072)	H^3	(+0.135)		
Propylene adsorption	Total	(-0.545)			Total	(+0.545)
	Subsurface layer	(-0.643)				
	Top layer	(+0.303)				
	Ni^1	(+0.020)			C^1	(+0.013)
	Ni^2	(+0.139)			C^2	(+0.085)
	Ni^3	(-0.138)			C^3	(-0.186)
					H^1	(+0.154)
					H^2	(+0.160)

3. Kinetic analysis

To indicate the kinetically favorable pathway for the main PDH in this study, we have compared the reaction rates of IS→TSA1 and IS→TSB1, the rate determining steps for C-H activation of pathways A and B.

Based on the transition-state theory (TST), a rate constant of an elementary reaction can be calculated from Eq. S1. [1]

$$k = A\ exp\left(-\frac{E_a}{k_B T}\right) \tag{S1}$$

where A is the pre-exponential/frequency factor. E_a is an activation energy of the elementary step, k_b is Boltzmann's constant, and T is temperature. The pre-exponential factor can be obtained from Eq. S2.

$$A = \frac{k_B T}{h} exp\left(\frac{\Delta S^{\ddagger}}{k_B}\right) \tag{S2}$$

where the entropy barrier, $\Delta S^{\ddagger}$, can be calculated from S_{TS}- $S_{reactant}$. E_a can be obtained from Eq. S3.

$$E_a = \Delta^{\ddagger} E_{DFT} + \Delta^{\ddagger} ZPE \tag{S3}$$

$$ZPE = \sum_{i=1}^{\#modes} \frac{h\nu_i}{2} \tag{S4}$$

$\Delta^{\ddagger}E_{DFT}$ and $\Delta^{\ddagger}$ZPE denote the energy barrier from DFT calculation and the zero point energy barrier, respectively. *h* and ν_i are Plank's constant and the vibrational frequency of *i* mode.

In this study, the reactions rates of IS→TSA1 and IS→TSB1, which are the rate determining steps for C-H activation of pathways 1A and 2A, are defined as k^{TSA1} and k^{TSB1}, respectively. It is to be noted that these two elementary steps have the same initial state (IS), therefore the ratio of k^{TSA1} and k^{TSB1} can be obtained by Eq. S5 or S6.

$$\frac{k^{TSA1}}{k^{TSB1}} = \frac{A^{TSA1}}{A^{TSB1}} exp\left(-\frac{\left(E_a^{TSA1} - E_a^{TSB1}\right)}{k_B T}\right) \tag{S5}$$

$$\frac{k^{TSA1}}{k^{TSB1}} = exp\left(\frac{S^{TSA1} - S^{TSB1}}{k_B}\right) exp\left(-\frac{\left(E_{DFT}^{TSA1} + ZPE^{TSA1} - E_{DFT}^{TSA1} - ZPE^{TSA1}\right)}{k_B T}\right) \tag{S6}$$

By neglecting entropy contributions from the translational and rotational degree of freedom, the entropy of the adsorbed intermediate can be estimated from vibrational contribution, S_{vib}, in Eq. S7 and S8.

$$S \approx S_{vib} = k_B \sum_{i=1}^{\#\ modes} \frac{h\nu_i}{2} \left(\frac{x_i}{e^{x_i} - 1} - \ln(1 - e^{-x_i}\right) \tag{S7}$$

$$x_i = \frac{h\nu_i}{k_B T} \tag{S8}$$

As a result, the calculated k^{TSA1}/k^{TSB1} values in range of 298K to 900K signify that pathway A is more kinetically preferable than another pathway (see Table S4).

Table S4 Comparison of k^{TSA1}/k^{TSB1} at different temperature

T (K)	k^{TSA1}/k^{TSB1}
298	2.05×10^{4}
400	4.87×10^{3}
500	2.12×10^{3}
600	1.23×10^{3}
700	8.34×10^{2}
800	6.24×10^{2}
900	4.99×10^{2}

References:

[1] Gokhale, A. A.; Kandoi, S.; Greeley, J.P.; Mavrikakis, M.; Dumesic, J.A. Molecular-level Descriptions of Surface Chemistry in Kinetic Models using Density Functional Theory. Chem. Eng. Sci. **2004**, *59* (22-23), 4679-4691.