

A DFT Study of Neopentane Hydrogenolysis and Isomerization on Pd(111) and Pt(111)

BY

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THESIS

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Table of Contents

SUMMARY	iv
1. INTRODUCTION	1
2. METHODS	6
3. RESULTS AND DISCUSSION	7
3.1 Dehydrogenation	7
3.2 Hydrogenolysis	12
3.3 Isomerization	17
3.3 Relationship between hydrogenolysis and isomerization	22
4. CONCLUSION	26
REFERENCES	28
Appendix A	33
Appendix B	34
Appendix C	35
VITA	36

SUMMARY

Using Density Functional Calculations, we examined hydrogenolysis and isomerization of neopentane on Pd(111) and Pt(111). In general, a lower activation energy is observed on the Pt(111) surface, which is in agreement with the experimental activity for the two metals. From the calculated reaction barriers, $\alpha^2\gamma^2$ -diadsorbed intermediate poses the lowest barrier for both hydrogenolysis and isomerization reactions for Pd(111) which is 1.06 eV and 1.63 eV respectively, indicating isomerization and hydrogenolysis occur through the same intermediate and compete with each other. In contrast, on Pt(111) the α^2 -mono-adsorbed intermediate has the lowest activation barrier for isomerization (1.27 eV) while $\alpha^2\gamma$ -di-adsorbed intermediate has the lowest activation barrier for hydrogenolysis (1.17 eV) indicating that isomerization and hydrogenolysis happen at different dehydrogenation levels on Pt(111). From the calculated barriers, we can partially rationalize the product selectivity for Pd and Pt catalysts. To conclude, neopentane isomerization and hydrogenolysis can follow the same mechanism as dehydrogenation of ~ 4 H will greatly reduce reaction barriers. However, unlike hydrogenolysis, isomerization through α^2 -mono-adsorbed intermediate may also play an important role on Pt(111).

1. INTRODUCTION

Fossil fuels will continue to be the most important source of energy for the foreseeable future.¹ However, due to environmental concerns surrounding their use, stricter regulation will be expected to be imposed on production, processing and use of hydrocarbon fuels. Thus, highly-refined fuels which maximize efficient energy extraction during conversion will increase in importance.¹ Hydrocarbon isomerization reactions are of high importance as they allow for tuning of octane/cetane numbers which determine engine performance. However, hydrocarbon isomerization is often accompanied by deleterious hydrogenolysis reactions which result in a yield loss through the formation light gas products. Thus, it is of great value to understand the mechanisms of hydrocarbon isomerization and hydrogenolysis on metal catalysts.

Typical metal hydrocarbon isomerization catalysts used for fuel reforming utilize late d-band transition metals such as Pt, Pd; commercial catalysts also employ selectivity promoting metals such as Sn and Re. Metal catalysts supported on acidic supports, also called bifunctional catalysts, are widely applied in industry. It is generally believed that transition metal only facilitates dehydrogenation and hydrogenation while the acid support promotes formation of carbenium ion through which isomerization occurs. A detailed review on alkane isomerization is presented by Ono.² In several early experimental studies,^{3,4,5} Gault et al. showed a common cyclopentane intermediate is involved in both hexane hydrogenolysis and isomerization. They also suggested hexane may also perform a skeletal rearrangement (isomerization) to form 2,3-di-methylbutane through a α,γ -adsorbed intermediate on platinum films. A similar proposal for alkane isomerization was made by Anderson and Avery⁶ (and later by Ptak and Boudart⁷) in which the hydrocarbon must be α,γ -di-adsorbed with one sp^2 carbon forming a double bond with a surface atom (and one sp^3 carbon forming a single bond with the surface) and then isomerization takes

place through a ring closure – ring opening mechanism on the surface such that the gamma carbon attaches to the alpha carbon.

It is often impractical to study the relationship between isomerization, hydrogenolysis and metal function in fuel reforming with real, complex feeds due to experimental difficulties and the extensive reactions network that will result. Therefore, surrogate or model compound studies are typically employed.⁸⁻¹⁴ In addition to hydrogenolysis and isomerization of n-alkanes, ring opening of cycloalkanes such as methylcyclohexane is of high interest due to its importance in hydrocarbon reforming. Most recently, Lercher et al.¹⁵ conducted studies of methylcyclohexane over supported iridium particles in order to determine the interplay between endocyclic and exocyclic C–C bond cleavage pathways with different ensemble size requirements as exocyclic C–C cleavage need a larger ensemble size. They later examined ring opening of cyclopentane on alumina-supported Pt particles with different Cl contents, indicating particle size effects stem from intrinsic rate constants (i.e. electronic effects) rather than coverage effects.¹⁶ Neopentane conversion has also been frequently examined for hydrogenolysis and isomerization because no olefins or carbenium ions which are common products of side reactions can be formed and therefore analysis is simplified.^{7,17-20} In addition the support is not involved in the observed chemistry due to removal of a carbenium mechanism for neopentane. Neopentane hydrogenolysis produces isobutane and methane initially. However, further hydrogenolysis may produce propane and ethane as well as additional methane. Isomerization produces isopentane initially, but a second isomerization step may produce n-pentane. Of course, isomerization products may also undergo hydrogenolysis (or vice versa). The full reaction network is presented in Figure 1.

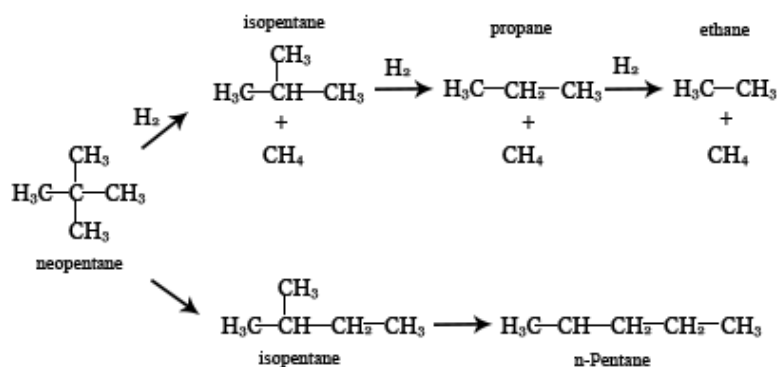


Figure 1: Neopentane reaction pathways

Neopentane hydrogenolysis/isomerization has been widely studied on Pd and Pt.^{6,7,17-22} Our recent study²⁰ uses neopentane isomerization to study the effects of geometric and electronic effects. For both Pt and Pd the isomerization selectivity increased as the particle size increased. Furthermore, the smallest Pt and largest Pd particles were found to have similar selectivity despite having significantly different structures. In fact, the isomerization selectivity was found inversely correlate with strength of adsorption of CO, indicating that the CO chemisorption energy could be used as a simple descriptor of the isomerization selectivity. The fact that the CO chemisorption energy could be correlated with the isomerization selectivity across particle sizes and type of metal implies the mechanisms for both isomerization and hydrogenolysis are equivalent at low-coordinate and high-coordinate sites.²⁰ Also, the relative activity of hydrogenolysis and isomerization is dependent solely on the electronic structure of the metal. Therefore we have used DFT calculations to try to test this hypothesis and determine how the binding strength (which can be related directly to the metal d-band center) controls selectivity.

To gain insight into the mechanism of hydrocarbon isomerization on metal catalysts, DFT calculations have been utilized recently in several investigations of alkane hydrogenolysis. Rosch and coworkers performed DFT studies^{8,9,23} of ring-opening

reaction of methylcyclopentane on Pt, Pd, Rh and Ir catalysts. Three possible products are 2-methylcyclopentane (2MP), 3-methylcyclopentane (3MP), and n-hexane. 2MP and 3MP are produced through a $\alpha^2\beta^2$ -di-adsorbed intermediate in agreement the mechanism proposed by Gault et al.³ Due to the substituted methyl group, the $\alpha^2\gamma$ -di-adsorbed intermediate is formed to produce n-hexane. Rosch et al. suggested a migration of adsorption site occurs before C-C bond breaking due to internal ring stress. This migration step significantly reduces the overall hydrogenolysis barrier. Calculated results show that the barrier height for dehydrogenation steps follows the trend: Ir(111) < Rh(111) < Pt(111) < Pd(111), whereas C-C rupture followed a slightly different trend: Rh < Ir < Pt < Pd. Furthermore Rosch et al found that at step sites of Pt surfaces, Pt(211), n-hexane formation is more favorable than branched hexanes due to formation of a low barrier adsorbed intermediate.

In a combined experimental and computational study Iglesia et al.^{10,11} showed that entropic considerations may dominate over reaction enthalpy when determining the location and rate of C-C bond cleavage. Flaherty et al performed a detailed analysis of the reaction kinetics which suggested that before hydrogenolysis may occur, linear alkanes (C₂-C₁₀) must lose ~4 hydrogen atoms from its backbone. Later, the same group employed DFT calculations to determine at which point C-C cleavage was favored over C-H cleavage. For ethane hydrogenolysis over Ir(111), the key intermediate was found to be HCCH (acetylene), in agreement with the previous kinetic study that suggested 4 Hs must be removed before hydrogenolysis of n-alkanes. However, Iglesia et al did not discuss selectivity to competing isomerization reactions (and of course in the case of ethane, there is no competing reaction other than dehydrogenation). In their most recent paper,²⁴ they claimed C-C bond breaking with alkyl substitution demand further dehydrogenation than those without alkyl substitution in ring-opening reactions on Ir. Therefore we will herein attempt to extend the work of Rosch, and Iglesia and determine

if branched alkanes (specifically the unique case of neopentane) behave differently than cycloalkanes or linear alkanes in hydrogenolysis. Meanwhile, isomerization is included to explore the reaction relationship. In this work we use DFT method to explore the mechanisms of neopentane hydrogenolysis and isomerization on Pd(111) and Pt(111). A full pathway analysis has been performed on both surfaces and related back to the experimental results of Childers et al²⁰.

2. METHODS

All calculations were performed using Vienna ab initio Simulation Package (VASP),²⁵,²⁶ employing the projector augmented wave (PAW)^{27,28} pseudopotentials with a cutoff energy of 500 eV. The electron-charge correlation was treated within the spin polarized general gradient approximation (GGA) and the Perdew-Becke-Ernzerhoff (PBE) functional²⁹⁻³¹. The Brillouin zone was sampled using a 3×3×1 k-point mesh³². The DFT-D2³³ method in VASP is used to account for the ν DW interactions. For Pt, we use C_6^{pt} = 42.66 nm⁶mol⁻¹ as determined by Balbuena et al.³⁴

The Pd and Pt models consist of four layers slabs with 18 Å of vacuum space between images; the cell size was 4×4. The bottom two layers are held fixed while the top two layers are allowed to relax. Geometry optimizations were considered to be converged when the force on each atom is less than 0.025 eV / Å. The nudged elastic band (NEB)^{35,36} method was used to get the transition state of the reactions. The transition state is identified as the maximum energy state along the minimum energy path. All transition states were converged such that tangent forces are <0.05 eV/Å. Each optimized transition state structure is confirmed through a normal mode analysis to ensure that only a single mode with an imaginary frequency exists. Vibrational calculations are performed by a diagonalization of the Hessian matrix created from the numerical second derivative of the energy with respect to the reaction coordinate.

3. RESULTS AND DISCUSSION

For elementary steps of neopentane conversion, we only examined dehydrogenation, hydrogenolysis and isomerization. Rehydrogenation of adsorbed intermediates has not been explicitly examined but is effectively included as hydrogenation events are simply the reverse reactions of dehydrogenation steps and are not likely to be the rate-limiting step. Also we have limited our analysis to a single hydrogenolysis or isomerization step such that the only product for isomerization would be isopentane and the only products for hydrogenolysis would be methane and isobutene (i.e. we did not calculate multiple hydrogenolysis or isomerization steps).

3.1 Dehydrogenation

Neopentane only weakly adsorbs to metal surfaces with an adsorption energy of -0.91 eV on Pt(111) and -1.17 eV on Pd(111) primarily due to van der Waals interactions. For the first dehydrogenation step, in the initial state, neopentane sits above the metal surface. A C-H bond may be broken on any of the CH₃ groups to form a, *CH₂C(CH₃)₃ group bonded to an atop metal site, leaving H adsorbed in its most favorable site, a 3-fold hollow site. In transition state, C atom and H atom is both bonded to metal surface as the C-H bond is broken. The reaction pathway for first dehydrogenation is shown in Figure 2. Experimental studies^{37,38} have shown the diffusion of H on Pd(111) and Pt(111) have very low activation barrier. Therefore, we neglect the effect of H between each subsequent dehydrogenation step and assume H atoms diffuse away from the hydrocarbon such that they will not affect further dehydrogenation steps (or isomerization or hydrogenolysis). At typical temperatures for neopentane conversion, hydrogen will rapidly recombine and desorb from the surface as it is bound with an adsorption energy of less than 0.5 eV on both Pt(-0.46eV)³⁹ and Pd (-0.39 eV)⁴⁰.

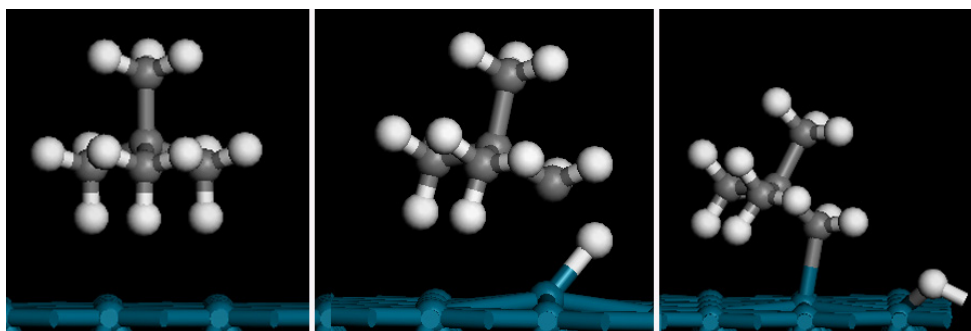


Figure 2: Initial state, transition state and final state for first dehydrogenation

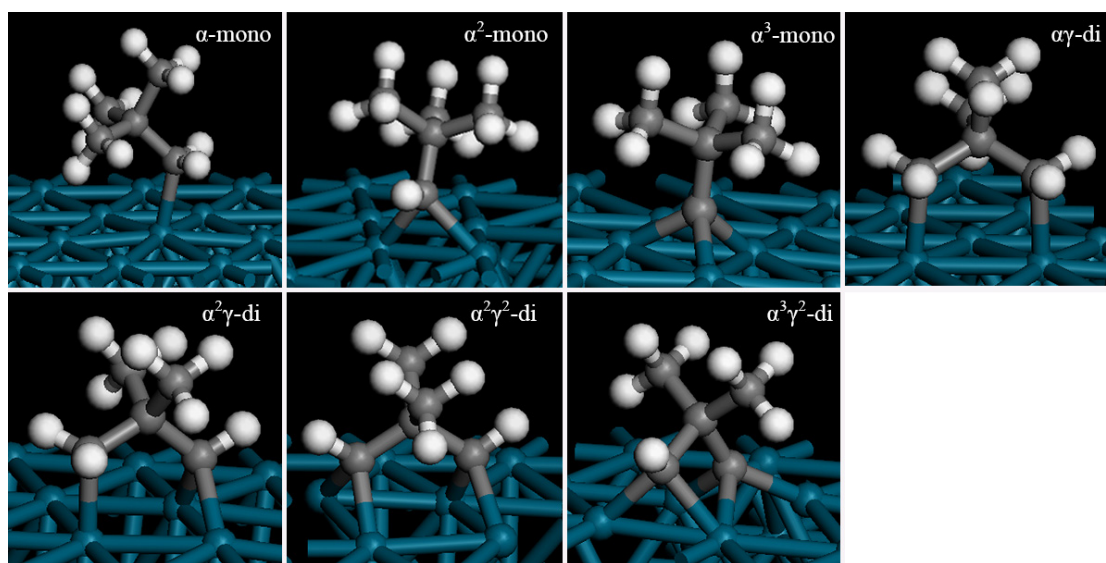


Figure 3: Intermediate structures after through various stages of dehydrogenation

After the first dehydrogenation event, there are two schemes for further dehydrogenation: H removal from the same C atom (α -elimination) or H removal on an adjacent C atom (β -elimination). Previous theoretical studies^{41,42} reported that β -elimination is favored for n-alkane over α -elimination on Pd(111) and Pt(111). Neopentane has unique structure where the central C is bonded with four geometrically identical methyl groups. Thus, β -elimination is not possible. Instead, further dehydrogenation occurs on another methyl group spaced apart by the central C atom, γ -elimination. Due to the similarity of β -elimination and γ -elimination, we assume γ -elimination will also be favored

over α -elimination. However, here we consider both α - and γ -elimination in order to examine hydrogenolysis and isomerization after dehydrogenation. For α -elimination, we examine cases for the removal of up to 3 H from the same C atom (i.e. complete dehydrogenation of the α -carbon). For γ -elimination, we calculated the energetics of steps for the removal of up to 5 H atoms from two different C atoms. Note we didn't consider γ -elimination after 2 or 3 α -elimination steps because the γ -C atom is far from the metal surface and barrier is expected to be high. All obtained intermediates are shown in Figure 3. We also did not consider cases where more than 2 C's are attached to the metal surface. Isomerization and hydrogenolysis are calculated for each of these intermediates. One structure worth noting is $\alpha^2\gamma^2$ -tetra-adsorbed intermediates. Both Rosch and Iglesia identify it as the optimal one for methycyclopentane and ethane hydrogenolysis respectively. Each C atom bonded with metal surface via two C-X (X=Pt, Pd) bond in a parallel fashion forming a diamond shape between the surface and the XC-C-CX skeleton of neopentane. It is interesting to note that the two metal atoms in the surface bonded to the molecule are pulled out of the surface plane a little bit (0.30 Å for Pd and 0.15 Å for Pt). This reflects a very strong bonding between C and metal atom. This phenomenon is not observed in any intermediates with less than 4 H removed.

Table 1: Reaction data for neopentane dehydrogenation steps

#	Reaction Steps	Pd(111)		Pt(111)	
		$\Delta E/\text{eV}$	E_a/eV	$\Delta E/\text{eV}$	E_a/eV
1	$\text{C}_5\text{H}_{12} \rightarrow \text{H}^* + {}^*\text{CH}_2\text{C}(\text{CH}_3)_3$	-0.05 ⁴³	1.16 ⁴³	-0.25	0.92
2	$\text{C}_5\text{H}_{11}^* \rightarrow \text{H}^* + {}^*\text{CHC}(\text{CH}_3)_3$	0.01	1.41	0.17	0.8
3	$\text{C}_5\text{H}_{11}^* \rightarrow \text{H}^* + {}^*\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2^*$	0.16 ⁴³	0.98 ⁴³	-0.11	0.63
4	$\text{C}_5\text{H}_{10}^* \rightarrow \text{H}^* + {}^*\text{CC}(\text{CH}_3)_3$	-0.91	0.46	-0.99	0.44
5	${}^*\text{C}_5\text{H}_{10}^* \rightarrow \text{H}^* + {}^*\text{CHC}(\text{CH}_3)_2\text{CH}_2^*$	-0.01	1.14	0.11	0.95
6	${}^*\text{C}_5\text{H}_9^* \rightarrow \text{H}^* + {}^*\text{CHC}(\text{CH}_3)_2\text{CH}^*$	0.2	1.41	0.2	0.76
7	${}^*\text{C}_5\text{H}_8^* \rightarrow \text{H}^* + {}^*\text{CC}(\text{CH}_3)_2\text{CH}^*$	0	0.92	0.32	1.21

Calculated results for dehydrogenation are summarized in Table 1. Dehydrogenation generally has rather low activation barriers for Pd(111) (ranging from 0.46 – 1.41 eV) and Pt(111) (ranging from 0.44 – 1.21) (Table1). For the α -H elimination series (Reaction steps 1, 2, 4), the reaction barrier decreases as the dehydrogenation level increases for Pt(111) while no trend is observed for Pd(111). In comparison, dehydrogenation through γ -elimination (Reaction steps 1, 3, 5, 6, 7) shows no apparent trends with the degree of dehydrogenation. The highest intrinsic barrier appears at the removal of the 4th H on Pd(111) and 5th H on Pt(111). Comparing α - and γ -elimination at the same dehydrogenation level (reaction steps 2 and 3), γ -elimination is more favorable by 0.43 eV (2nd H removal) on Pd and 0.17 eV (2nd H removal) on Pt, which is consistent with our hypothesis. However, data show elimination of the 3rd H through α -elimination is more favorable than through γ -elimination for both catalysts. It should be noted that

reaction step 4 is highly exothermic (-0.91 and -0.99 eV) and it is drastically different from all other hydrogenation steps which are only slightly exothermic or slightly endothermic. This indicates that dehydrogenation of the 3rd H will be highly preferred once two H atoms are already removed from the same C atom. Flaherty's work on ethane suggests up further dehydrogenating $^*HCCH^*$ is highly unfavorable ($E_{act} = 1.90$ eV) and the barrier is higher than hydrogenolysis by 0.73 eV. Reaction step 7 does show an increase in activation barrier for Pt, indicating that dehydrogenation may stop at the $\alpha^2\gamma^2$ intermediate. In the case of Pd, the barrier rises for the removal of the 4th C (reaction step 6). Nevertheless, we never observe this drastic difference between dehydrogenation and hydrogenolysis at this level. In fact, they are comparable (with maximum barrier difference within 0.3 eV). So, dehydrogenation on branched alkanes behaves differently than straight chain alkanes and the dehydrogenation barrier never increases dramatically as in the case for C_2H_2 intermediates dehydrogenating to CCH.¹¹

Comparing activation barriers between Pd(111) and Pt(111), Pt(111) generally has lower reaction barriers, indicating higher activity of Pt for dehydrogenation. This is consistent with Rosch's study⁸ on ring opening of methylcyclopentane. The exception to this pattern appears to be removal of the 5th H, which is unfavorable on Pt.

Norskov et al.⁴⁴ show that generally the activation barrier scales with the reaction energy for heterogeneous catalyst triggered surface reactions for systems with similar transition state geometries (e.g. hydrocarbon dehydrogenation events). This general rule is called Brønsted–Evans–Polanyi relation. Due to difference in transition state, we will expect approximate linear fit between reaction energy and activation barrier. Figure 4 shows both Pd(111) and Pt(111) can be fit to a linear relationship while Pt line has a lower slope. In conclusion, Pt(111) has a higher activity in dehydrogenation than Pd(111).

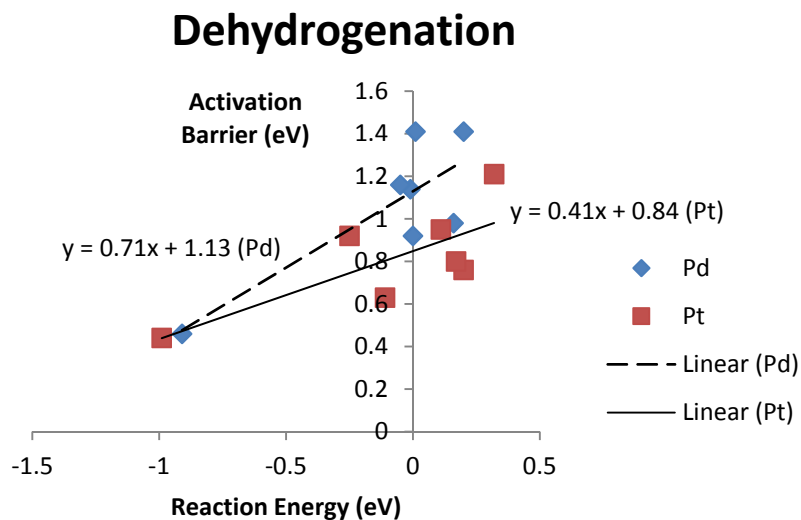


Figure 4: Dehydrogenation reaction enthalpy and activation energy relationship

3.2 Hydrogenolysis

Hydrogenolysis has been considered after every dehydrogenation step and results are summarized in Table 2. All final state structures and transition state structures are presented in Appendix A. In addition, a sample calculation of direct cleaving neopentane without dehydrogenation was tried and a barrier larger than 3.0 eV was obtained which is insurmountable in practical reaction.⁴³

Table 2: Reaction data for neopentane hydrogenolysis steps

#	Reaction Steps	Pd(111)		Pt(111)	
		ΔE /eV	E_a /eV	ΔE /eV	E_a /eV
8	$C_5H_{11}^* \rightarrow CH_2^* + C_4H_9^*$	0.63 ⁴³	1.98 ⁴³	0.01	2.55
9	$C_5H_{10}^* \rightarrow CH^* + C_4H_9^*$	0.54	1.5	-0.44	1.86
10	$*C_5H_{10}^* \rightarrow *CH_2^* + C_4H_8^*$	0.28	1.82	0.61	1.86
11	$C_5H_9^* \rightarrow C^* + C_4H_9^*$	1.24	2.49	1.11	2.56
12	$*C_5H_9^* \rightarrow CH_2^* + C_4H_7^*$	0.68	1.41	0.61	1.67
13	$*C_5H_9^* \rightarrow CH^* + C_4H_8^*$	-0.3	1.24	0.23	1.17
14	$*C_5H_8^* \rightarrow CH^* + *C_4H_7^*$	0.08	1.06	-0.04	1.21

Hydrogenolysis steps after α -elimination (reaction steps 8, 9, 11), generally have rather high reaction barriers (1.5 - 2.5 eV for Pd, 1.9 – 2.6 eV). No easily discernable trend correlating the activation barriers with the degree of dehydrogenation is observed. As previous section suggests dehydrogenating 3 Hs on the same C is highly favorable after α^2 -mono-adsorbed intermediate, hydrogenolysis at this level (reaction step 11) is, very difficult. It is highly endothermic (1.24 eV for Pd and 1.11 eV for Pt) and has highest reaction barrier for hydrogenolysis (2.49 eV for Pd and 2.56 eV for Pt). This high barrier may results from a formation of C atom direction bonded to metal surface via three C–metal bonds, similar to formation of a metal carbide which is not favorable for late d-band transition metals.⁴⁵

For hydrogenolysis after γ -elimination (reaction steps 8, 10, 12, 13, 14) where the molecule is bound to the surface via a second C, there is an approximate trend that as

dehydrogenation level increases, reaction barrier decreases. The lowest reaction barrier is observed after ~4 H are removed (4 for Pd (Figure 5), 3 for Pt). The barrier difference between reaction from mono-adsorbed and di-adsorbed intermediate is 0.44 eV for Pd and 0.65 eV for Pt. Since the dehydrogenation barrier is relatively low (<1.41 eV for Pd, <0.95 eV for Pt), dehydrogenation of at least 3 H atoms will proceed before hydrogenolysis on Pd(111) and Pt(111). This finding is consistent with Rosch's work²³ on methylcyclopentane and Flaherty's work with ethane.¹¹ As neopentane adsorbs on the metal surface, the original C-H bond is replaced with a C-X (X= Pt, Pd) bond which weakens corresponding C-C bond. For straight chain alkanes and cycloalkanes, dehydrogenation on both C atoms weakens the C-C bond they are sharing. However, in the case of the neopentane, the single adsorbed intermediate involves only one C from the C-C bond that is being cleaved in hydrogenolysis. Since the central C is not bound to the surface, the C-C bond in adsorbed neopentane intermediate is stronger than a similar species from an adsorbed intermediate from dehydrogenation of n-alkanes. In contrast, for a di-adsorbed intermediate, although the central C is still not bound to the surface, now the presence of a second metal surface bond weakens both C-C bonds. Our results show despite the lack of β coordination to the surface, neopentane still needs to bind to the metal surface through two different C atoms before hydrogenolysis can occur.

As was discussed in the dehydrogenation section, $\alpha^2\gamma^2$ -adsorbed intermediates have a strong bonding between C atoms and catalyst surface. Note that the length of the target C-C bond to be broken is 1.53 Å (as compared to 1.55 Å between a methyl group C and the central C in neopentane). Although in the $\alpha^2\gamma^2$ intermediate, 2 hydrogens have been removed from each C atom, the C-C bond doesn't contract much and retains the character of a single bond. This can partly account for the low activation barrier for hydrogenolysis. In Rosch's work, they suggest a migration step before the most favorable hydrogenolysis step for methylcyclopentane ring-opening reaction. However, this site

migration step is unlikely to occur for neopentane as the C-C bond doesn't compress much (only 0.02) and the second point of attachment is at the γ position as opposed to the β position. For example, the C-C bond distance in C_2H_4 is 1.34 Å and the C-C bond distance in C_2H_2 is 1.20 Å. Attempts to locate an alternate adsorption site were unsuccessful.

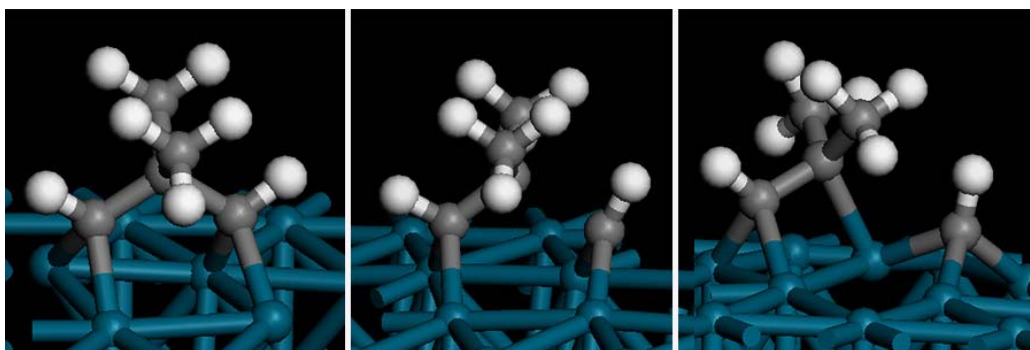


Figure 5: Initial state, transition state, final state for reaction step 14

As we can see from Table 2, hydrogenolysis of di-adsorbed intermediates requires a lower barrier than that of mono-adsorbed intermediates. Meanwhile, the lowest barrier difference between the α and γ pathways is 0.44 eV for Pd and 0.65 eV for Pt. We can safely conclude that hydrogenolysis through the γ pathway is the primary mechanism for neopentane hydrogenolysis. As mentioned above, this result is consistent with Rosch's work on cycloalkanes and Iglesia's work on straight chain alkanes. In addition to the weakening of the C-C bond, the presence of multiple C-M bonds, the lower barrier can also be explained by a more stable final structure (and therefore by analogy a more favorable transition state structure). As the calculations suggest, hydrogenolysis involves steps including elongation of the C-C bond, and formation of a new C-X (X=Pt, Pd) bond, which results in a C1 group and a C4 group. For the C4 group, γ -elimination intermediate generates a more stable structure as it has more than one bond to the catalyst surface. Similarly, the transition state for a di-adsorbed intermediate hydrogenolysis event is stabilized by C-M bonding for the C4 group compared to the transition state for a mono-bound intermediate, which has no

bonding at all (i.e. only the C1 group is continuously bound to the surface throughout the reaction).

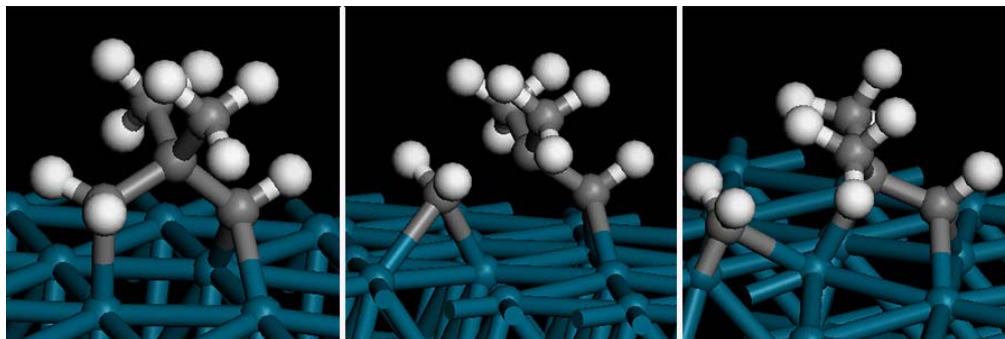


Figure 6: Initial state, transition state, final state for reaction step 12

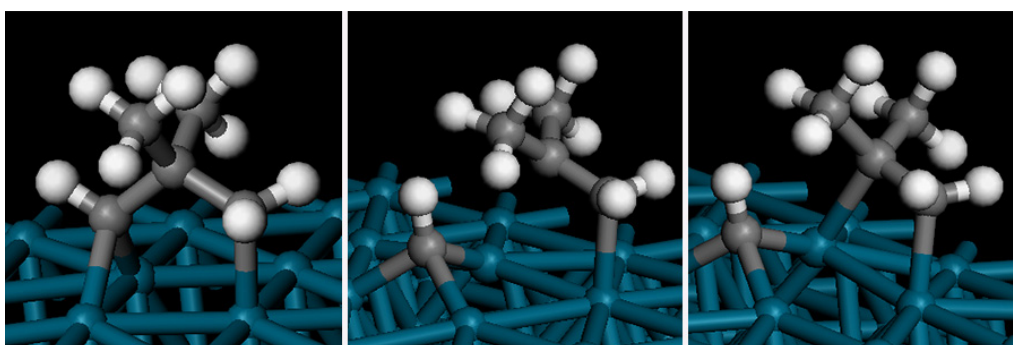


Figure 7: Initial state, transition state, final state for reaction step 13

Hydrogenolysis of the $\alpha^2\gamma$ -di-adsorbed intermediate has two directions, breaking C-CH₂ bond (reaction step 12, Figure 6) or breaking C-CH bond (reaction step 13, Figure 7). On both Pt and Pd, hydrogenolysis will preferred through cleavage of the C-CH bond than C-CH₂ with a barrier difference of 0.17 eV and 0.50 eV respectively. It appears that further dehydrogenation of the C-C bond is preferred until C is the final product. Despite their similar final structures, reaction step 13 has a more stable final structure than reaction step 12 as we can see from the reaction enthalpy. It can be deduced from the transition structures of reaction 12 and 13 that stabilizing the C1 group maybe is more important than stabilizing the C4 group.

To verify a Brønsted–Evans–Polanyi relation for hydrogenolysis, the calculated barriers and reaction energies are plotted in Figure 8. Data for Pd and most of the data for Pt can be fit to an approximate linear relationship between reaction energy and reaction barrier. There are two obvious outliers which are hydrogenolysis step 8 and hydrogenolysis step 9. Both of these outliers are pathways through an α intermediate. Their activation barriers are in the expected range but their reaction enthalpies are reduced by a margin. The current origin of the deviation in reaction enthalpies is unknown and further investigation is required. Overall, the reaction barrier for Pd and Pt are quite close for hydrogenolysis. Pd(111) is slightly more active than Pt(111) in hydrogenolysis.

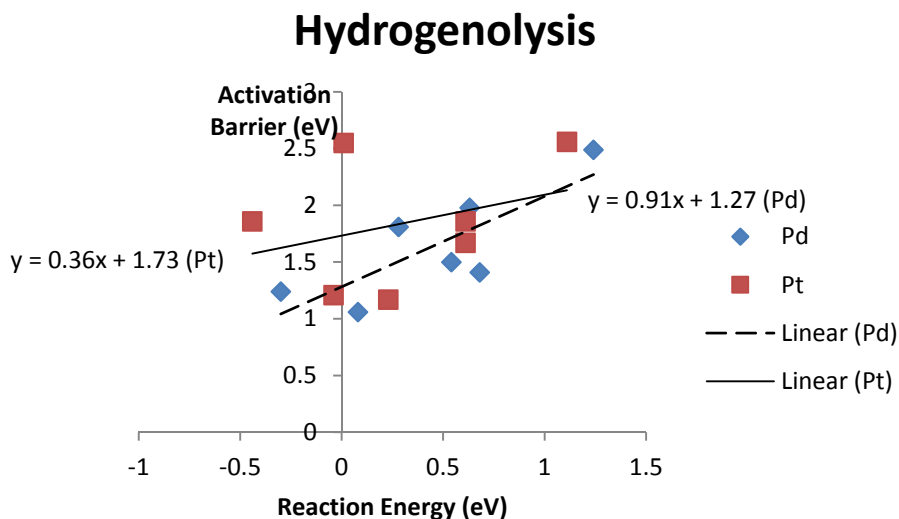


Figure 8: Hydrogenolysis reaction enthalpy and activation energy relationship

3.3 Isomerization

Table 3: Reaction data for neopentane isomerization steps

#	Reaction Steps	Pd(111)		Pt(111)	
		ΔE /eV	E_a /eV	ΔE /eV	E_a /eV
15	$C_5H_{11}^* \rightarrow ^*CH_3C(CH_3)CH_2CH_3$	0.47	1.97	-0.09	1.78
16	$C_5H_{10}^* \rightarrow CH_3C^*(CH_3)CH^*CH_3$	-0.3	1.73	-0.49	1.27
17 ⁴⁴	$^*C_5H_{10}^* \rightarrow ^*CH_2C(CH_3)CH_2CH_3$	-0.62 ⁴³	1.81 ⁴³	0.08	1.77
18	$C_5H_9^* \rightarrow CH_3C^*C^*(CH_3)CH_3$	0.57	2.5	1.34	2.29
19	$^*C_5H_9^* \rightarrow ^*CHC(CH_3)CH_2CH_3$	0.03	2.4	0.07	2.28
20	$^*C_5H_9^* \rightarrow ^*CH_2C(CH_3)CHCH_3$	-0.57	1.76	-0.5	1.4
21	$^*C_5H_8^* \rightarrow ^*CHC(CH_3)CHCH$	-0.5	1.63	-0.42	1.37

The reaction enthalpies and activation energies for isomerization are summarized in Table 3. All final state structures and transition state structures for isomerization are presented in Appendix B. For isomerization after α -elimination (reaction step 15, 16 and 18), no apparent trend exists between the dehydrogenation level and the reaction barrier. Though reaction steps 15 and 18 still have relatively high reaction barriers as compared to their hydrogenolysis counterparts, reaction step 16 through an α^2 -mono-adsorbed intermediate (Figure 9) exhibits a surprising low reaction barrier of 1.73 eV on Pd and 1.27 eV on Pt. The lowest barrier on Pd still happens for the $\alpha^2\gamma^2$ -di-adsorbed intermediate (Figure 10) with 1.63 eV. One explanation that accounts for this low barrier is that the final state is very stable compared to the other mono-adsorbed intermediates. As in the case for hydrogenolysis, reaction step 18 still has the highest isomerization barrier and is highly endothermic for both Pt and Pd, suggesting an aversion to isomerize after 3 H atoms are removed from the same C.

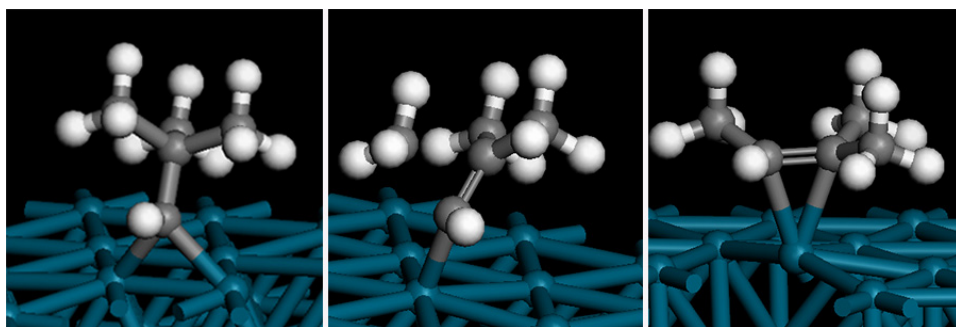


Figure 9: Initial state, transition state, final state for reaction step 16

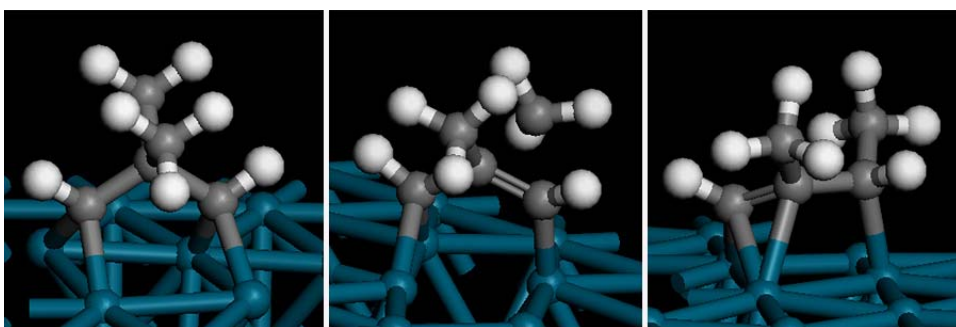


Figure 10: Initial state, transition state, final state for reaction step 21

For isomerization of di-adsorbed intermediates (reaction step 15, 17, 19, 20, 21), there is a clear trend that as dehydrogenation level increases, reaction barrier decreases with one exception, exception step 19 which can be excluded as it is only one isomerization direction after $\alpha^2\gamma$ -intermediate. It should be pointed out that the hydrogenolysis reaction series through di-adsorbed intermediates has a similar relationship. It can be concluded that dehydrogenation through γ -elimination up until 4 H atoms will benefit both hydrogenolysis and isomerization. It appears that, isomerization and hydrogenolysis have similar pathways through which they both possess a rather low barrier. This substantiates our conclusion in Childers et al.²⁰ that a single common intermediate is controlling the reactivity. Childers et al. suggested that the energy of the intermediate must scale with CO adsorption energy such that CO adsorption can be used

as a single descriptor to describe isomerization selectivity. This can only be true if the reaction site and reaction intermediate is a single configuration.

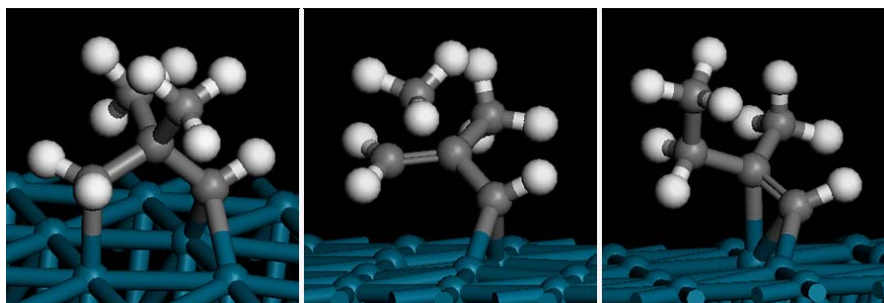


Figure 6: Initial state, transition state, final state for reaction step 19

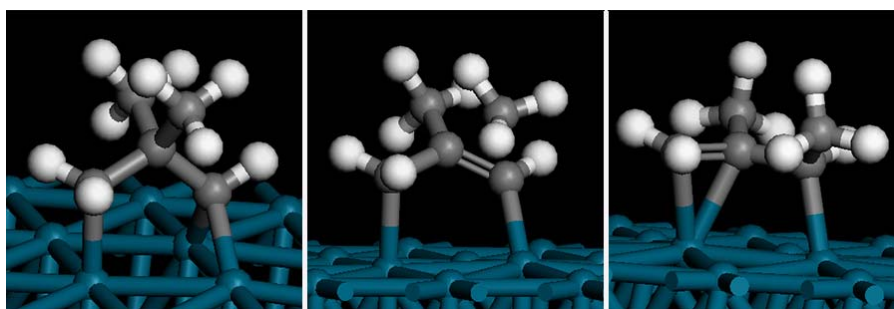


Figure12: Initial state, transition state, final state for reaction step 20

Similarly, isomerization can also take two pathways after $\alpha^2\gamma$ -di-adsorbed intermediate is formed: A methyl group can break from the central carbon and isomerize to form a bond to $^*\text{CH}$ (reaction step 19, Figure 11) or to $^*\text{CH}_2$ (reaction step 20, Figure 12). In the discussion of previous section, we conclude that for the $\alpha^2\gamma$ -di-adsorbed intermediate, hydrogenolysis tends to break the C-CH bond instead of C-CH₂ bond. In a similar way as for hydrogenolysis, isomerization tends to occur at $^*\text{CH}$ rather than at $^*\text{CH}_2$ with a barrier difference of 0.64 eV for Pd and 0.88 eV for Pt. Both hydrogenolysis and isomerization prefer to occur via the more dehydrogenated carbon than the less dehydrogenated carbon. To explain this preference, transition state structures are compared as shown in Figure 11 and Figure 12. The difference in the transition state structures between steps 19 and 20 is that the lower activation barrier structure (20) is bonded through 2 C atom instead of 1

C atoms. The barrier is likely lower because the C₄ fragment is more stable by maintain bonding to the metal surface with both C atoms throughout the transition state. Although hydrogenolysis and isomerization compete at same intermediate at each dehydrogenation step, their mechanisms are quite different. The isomerization generally involves elongation of the C-C bond and lengthening of the C-M bond followed by reformation of a C-C bond. In isomerization both the central carbon and the moving methyl group are not directly bonded to metal atom while for hydrogenolysis only the central C is not bonded to the surface. For hydrogenolysis, the bond that needs to be weakened is the C-C bond between the central C atom and the C atom which binds to metal surface while for isomerization the bond to be weakened is between the central C atom and a methyl group C that is completely unbonded to the surface. A smaller difference (only 0.1 eV) between isomerization for the α^2 -intermediate and $\alpha^2\gamma^2$ -intermediate is observed on both Pd and Pt as compared to hydrogenolysis (larger than 0.4 eV). This may suggest a different requirement of dehydrogenation for isomerization and hydrogenolysis despite the fact both reactions have lower barriers as the extent of dehydrogenation increases for di-adsorbed intermediates. The different requirement for dehydrogenation can also account for the fact that the lowest barrier intermediate for isomerization on Pt is the α^2 -mono-adsorbed intermediate instead of an $\alpha^2\gamma^2$ -di-adsorbed intermediate. Hydrogenolysis of mono-adsorbed intermediates is extremely unlikely, but for isomerization, both the mono-adsorbed and di-adsorbed intermediates may be of comparable importance. This results from a better stabilization of the transition state for the α -elimination pathway.

Both Pd(111) and Pt(111) can be fit to an approximately linear relationship between the activation barrier and the reaction enthalpy for isomerization as shown in Figure 13. The Figure shows that Pt(111) is expected to be more active in isomerization than Pd(111).

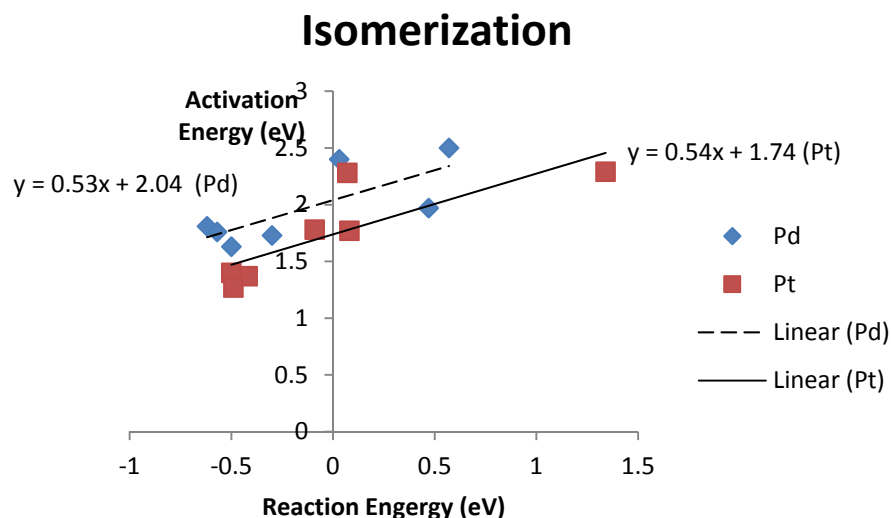


Figure 7: Isomerization reaction energy and activation energy relationship

3.3 Relationship between hydrogenolysis and isomerization

Combining the results from dehydrogenation, hydrogenolysis and isomerization, we can account for the higher selectivity for isomerization on Pt. While Pt and Pd have similar reaction barriers for hydrogenolysis, Pt has relatively lower reaction barriers for both dehydrogenation and isomerization.

To explore the relationship between hydrogenolysis and isomerization, we define dehydrogenation level as H atoms number removed from neopentane without regard to the H elimination scheme. The reaction barrier is plotted as a function of the extent of dehydrogenation in Figure 14. Both Rosch⁸ and Iglesia¹¹ suggest 4 H are removed before hydrogenolysis happens. In Figure 11, we can see clearly see trend that generally for di-adsorbed intermediates (for both hydrogenolysis and isomerization, on both Pt and Pd), the reaction barrier decreases with increase of dehydrogenation level. Reactions involving di-adsorbed intermediates reactions also will play a more important role than their corresponding mono-adsorbed intermediates as the barriers for reactions involving the di-adsorbed species are consistently lower. The only exception occurs for the isomerization

of mono-adsorbed series on Pt which have comparable reaction barriers to reactions involving di-adsorbed species. Comparing Pt and Pd, the reactions of di-adsorbed species have comparable barriers with differences of less than 0.2 eV for hydrogenolysis. Although the barriers generally decrease with increase of the degree of dehydrogenation, the isomerization barrier on Pt decreases with a small slope and dehydrogenation of 4 Hs, still does not significantly lower the barrier. For intermediates with a loss of 4 Hs, whether for Pt or Pd, isomerization has a higher barrier than hydrogenolysis. However, the barrier difference is much smaller for Pt (around 0.2 eV) than Pd (around 0.7 eV).

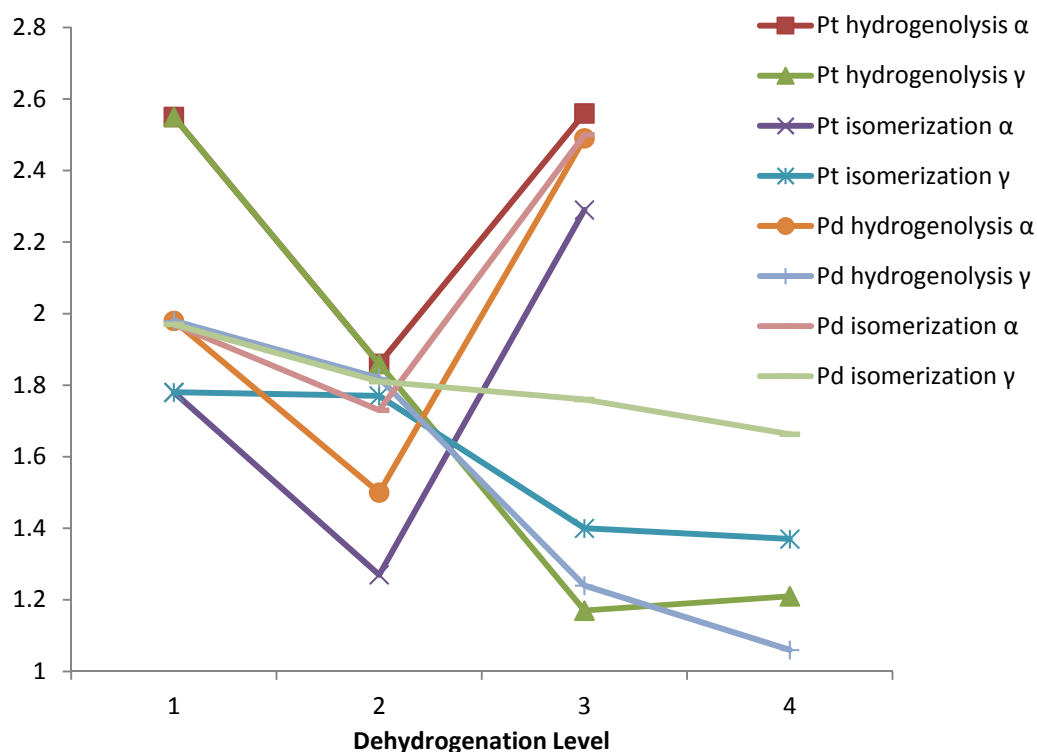


Figure 8: Relationship between dehydrogenation level and activation energy

Neopentane undergoes both hydrogenolysis and isomerization pathways. Both Pt and Pd exhibit a clear particle size effect which increasing particle size leads to higher isomerization selectivity with Pt having a significant higher selectivity than Pd at an equivalent particle size. Both Childers et al.²⁰ and Foger et al.¹⁹ have suggested that

isomerization will dominate neopentane conversion on Pt(111). However, we find that the lowest hydrogenolysis barrier is actually still lower than the isomerization barrier regardless of the degree of dehydrogenation. It is not clear if we have not located the proper mechanism for isomerization (i.e. a pathway with a lower barrier exists) or if DFT is not capable of properly assessing the energetics of this reaction or if the error stems from some other reason. We conducted a simple kinetic calculation for this simple step at 275 °C; this difference will result in an isomerization selectivity of 3.9%.

From energy profile of the reaction pathways on Pt(111) in Figure 15, dehydrogenation is favored over hydrogenolysis and isomerization over the whole range of dehydrogenation steps examined. In fact for the $\alpha^2\gamma^2$ -di-adsorbed intermediate, all three reactions have comparable barriers (dehydrogenation barrier is equivalent to the hydrogenolysis barrier, the isomerization barrier slightly higher than the other two). In contrast, for Pd(111), the potential energy surface shown in Figure 1, Appendix C, indicates that dehydrogenation is favored over hydrogenolysis and isomerization by a large amount until 3 H atoms are removed. For the $\alpha^2\gamma$ -di-adsorbed intermediate, hydrogenolysis is preferred over further dehydrogenation by a small amount. In fact for the $\alpha^2\gamma$ -di-adsorbed intermediate, all three reactions have comparable barriers (isomerization is only slightly higher.) Further dehydrogenating the 5th H atom results in a larger energy difference between dehydrogenation and hydrogenolysis/isomerization.

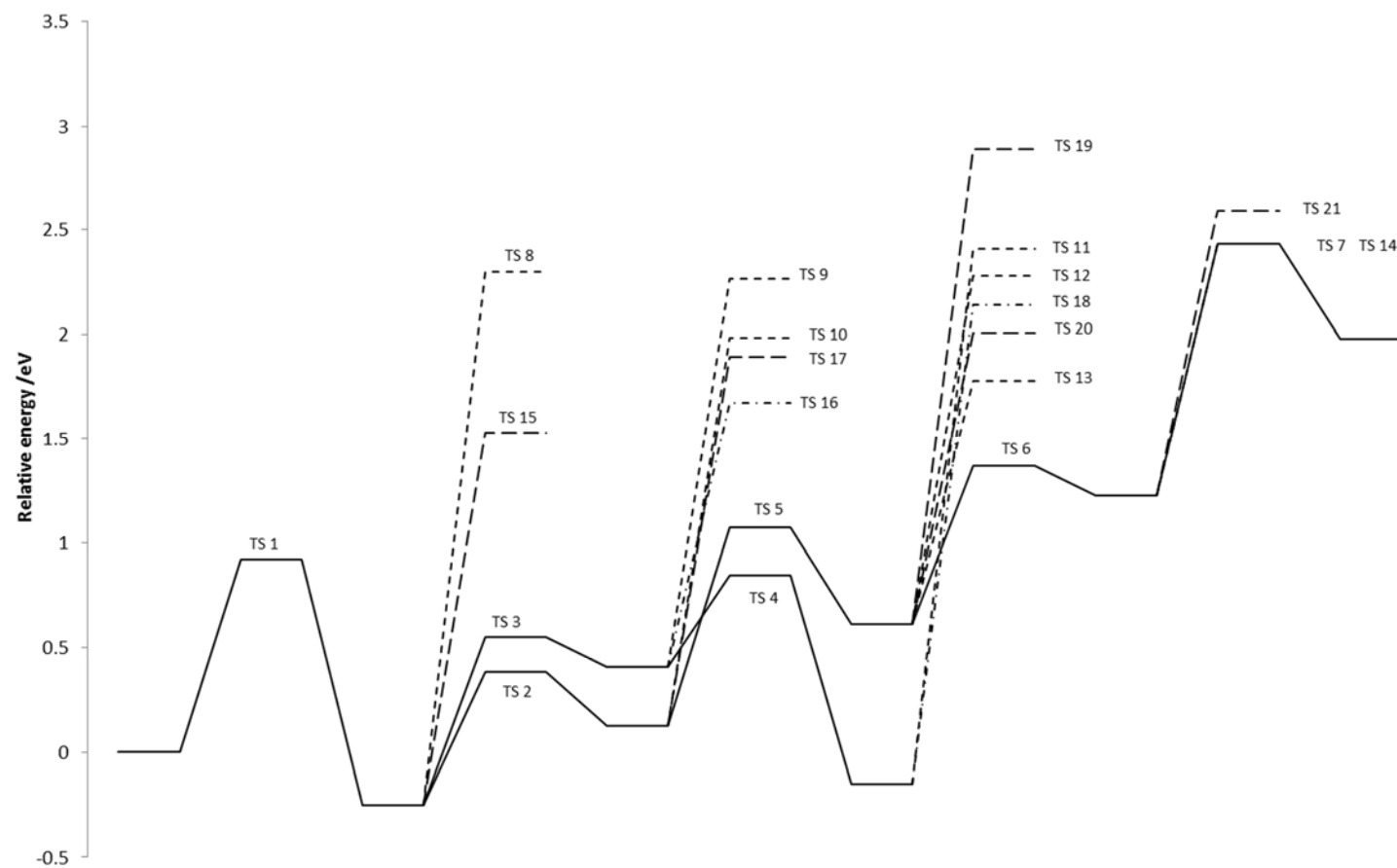


Figure 9: Energy profile for neopentane reaction on Pt(111)

4. CONCLUSION

We have studied the conversion of neopentane using DFT calculations. Activation barriers and reaction energies for neopentane dehydrogenation, hydrogenolysis and isomerization have been calculated on Pd(111) and Pt(111). Transition structures of each step are also obtained.

Our results shows that generally the activation barriers for these processes on Pt(111) are lower than Pd(111). Also, our calculation corroborate that neopentane tends to undergo hydrogenolysis and isomerization after 3 or 4 H were removed from two C atoms in most cases. Hydrogenolysis and isomerization of these di-adsorbed intermediates benefit from a more stable transition state and final structure. This is in good agreement with previous DFT studies examining n-alkanes and methylcyclopentane. Meanwhile it suggests that hydrogenolysis and isomerization may be mediated by a same intermediate and explains why a single descriptor such as the CO adsorption energy can be used to correlate neopentane isomerization selectivity. While hydrogenolysis will dominantly occur through di-adsorbed intermediates, isomerization may possess two important pathways through both mono-adsorbed and di-adsorbed intermediates. On basis of the calculated barriers, we can rationalize the higher selectivity of isomerization on Pt to Pd, that is, Pt has a lower isomerization activation energy similar but a comparable hydrogenolysis activation energy.

Though our work shed light on mechanism of alkane hydrogenolysis and isomerization, more work remains to be done. Isomerization and hydrogenolysis mechanisms involving intermediates with more extensive degrees of dehydrogenation (more than 5) were not addressed in this work. In addition, the surface coverage effect of the reactants is not considered in this work. However, high H surface coverage or high neopentane coverage may affect the reaction mechanism as reaction barriers are expected to be coverage dependent. Furthermore, in order to examine particle size effect

on alkane hydrogenolysis and isomerization, other catalyst surface, like (211), should also be examined. It should also be mentioned that other isomerization mechanisms could also be viable pathways. Fogar et. al¹⁷ proposed a tri-adsorbed intermediates which well explains the particle size effect observed on catalysts surface since this intermediate can only form on a more low coordinate surface. Isomerization by a ring-closure ring-opening (discussed in the introduction section) mechanism may need additional investigation .¹⁸

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Appendixes

Appendix A

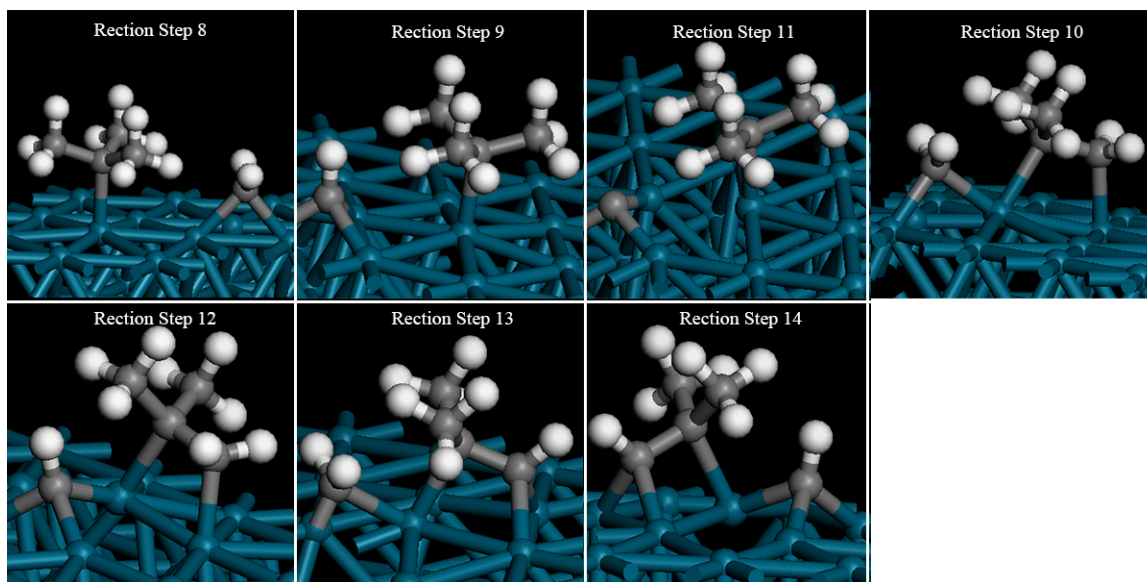


Figure 1: Final state structures for all hydrogenolysis reactions

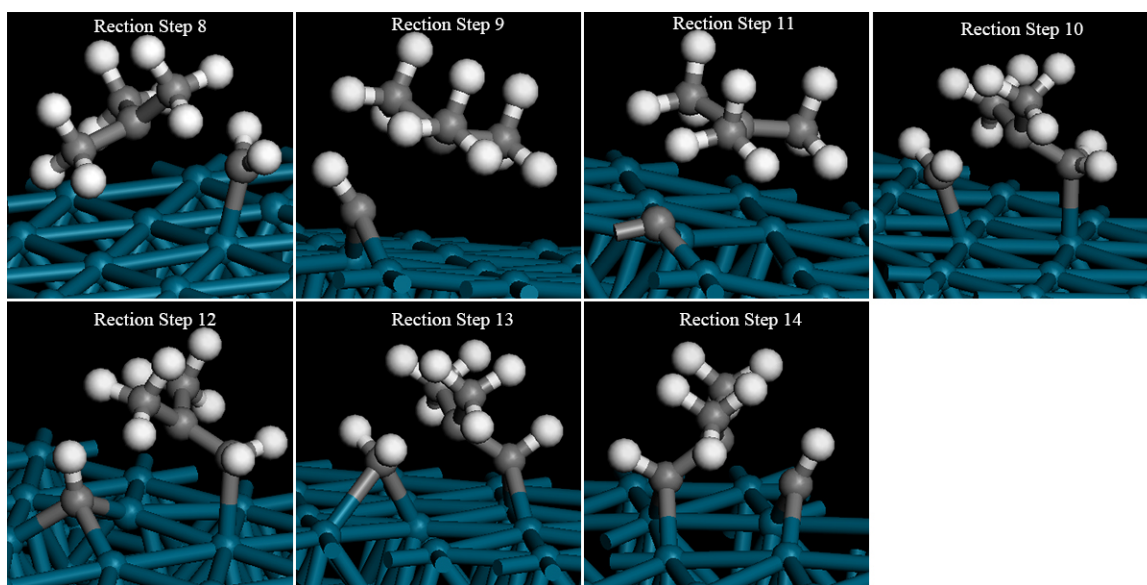


Figure 2: Transition state structures for all hydrogenolysis reactions

Appendix B

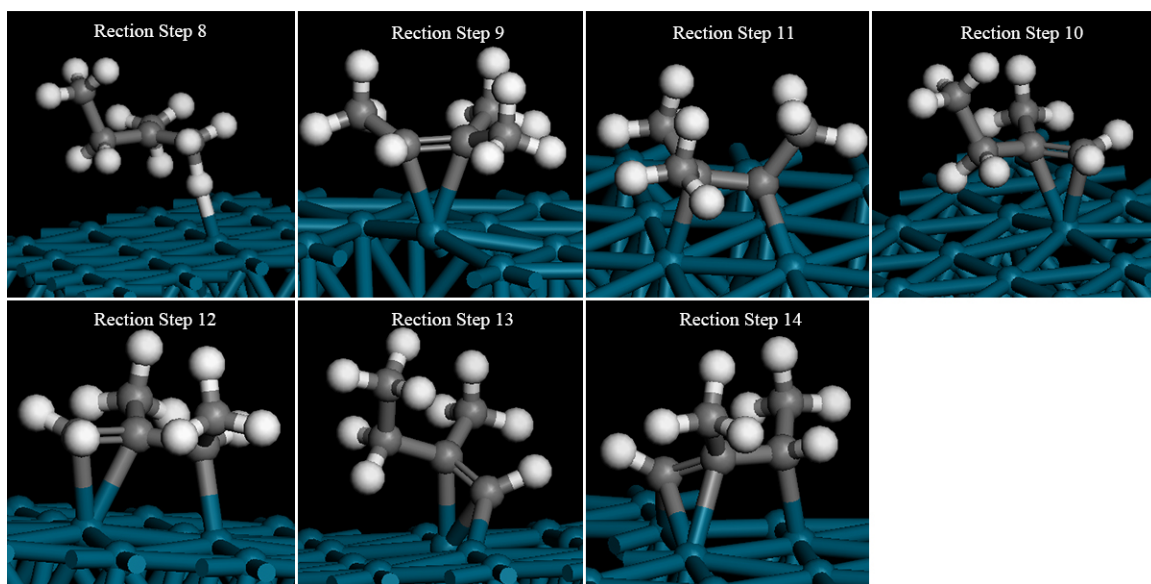


Figure 1: Isomerization final state structures.

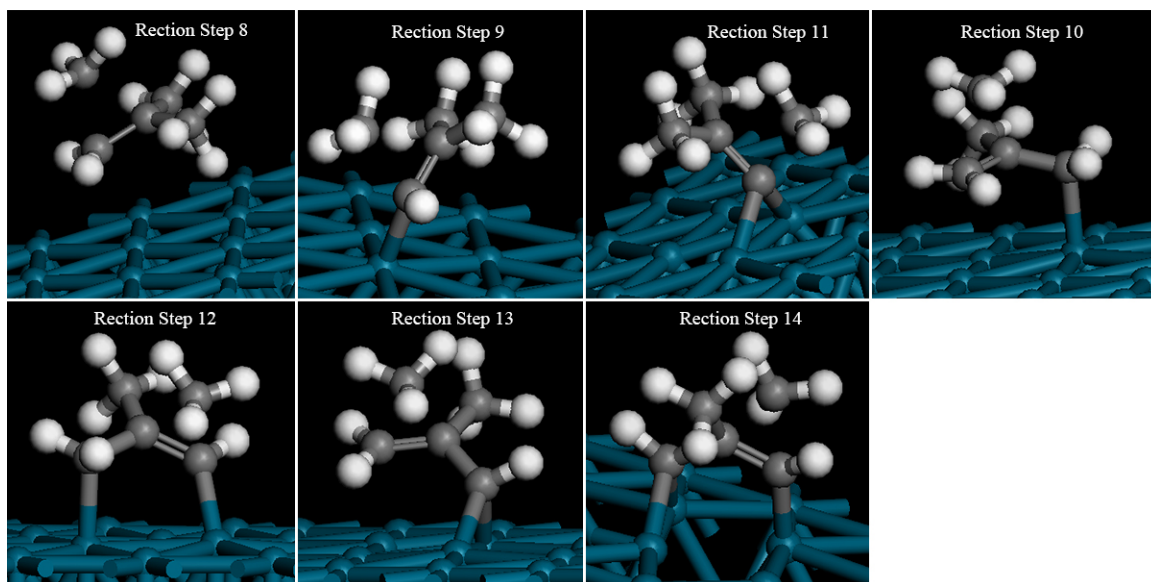


Figure 2: Isomerization transition state structures.

Appendix C

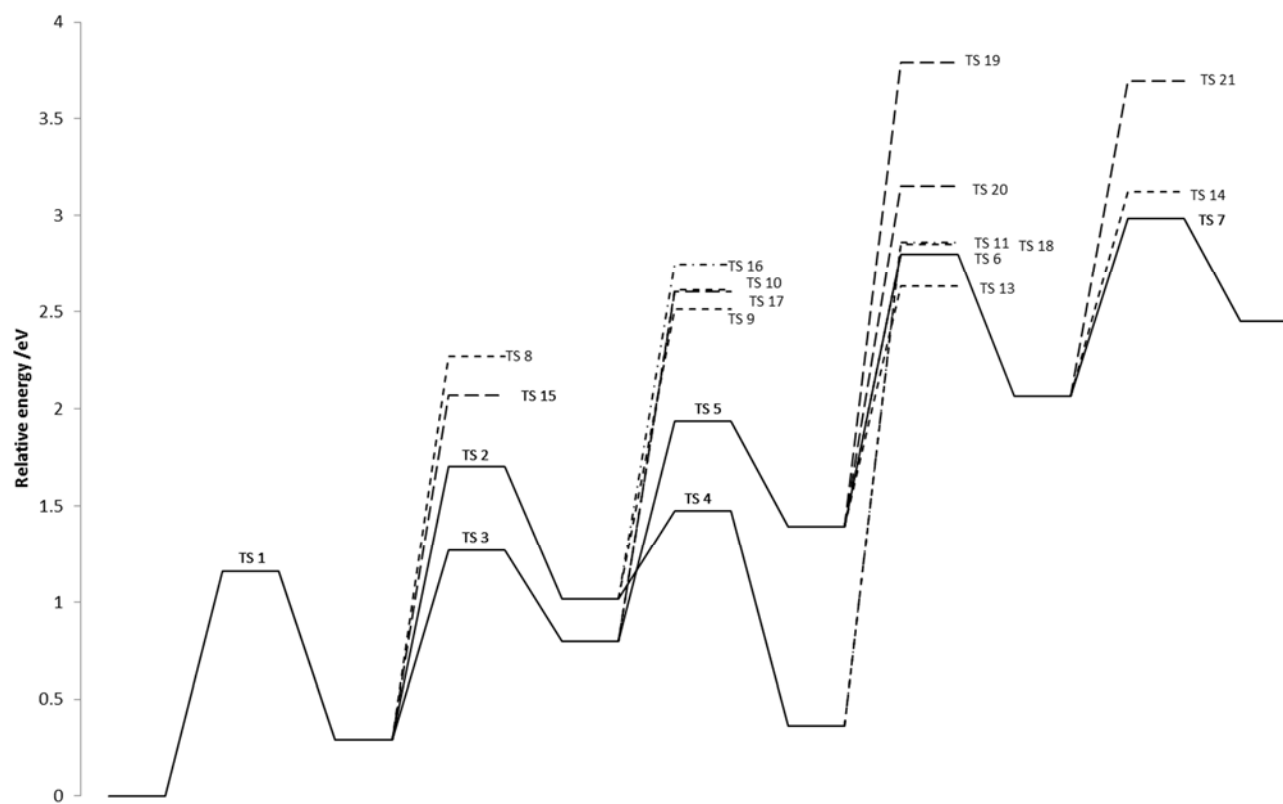


Figure 1: Energy profile for neopentane reaction on Pd(111)

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