

Reactions of 1-Butene and *cis*-2-Butene on Platinum Surfaces: Structure Sensitivity of *cis*-2-Butene Isomerization

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The hydrogenation and isomerization of 1-butene and *cis*-2-butene molecules are studied on platinum foil and single crystal (111), (100), and the stepped (755) surfaces at 300–350 K. In the presence of hydrogen, 1-butene and *cis*-2-butene are hydrogenated to butane. In addition, 1-butene is isomerized to *cis*- and *trans*-2-butenes, while *cis*-2-butene is converted to *trans*-2-butene. With a hydrogen pressure between 7 and 500 Torr, and a butene pressure of 3.5–70 Torr, both butene hydrogenation and isomerization rates exhibit a near-first-order dependence on the hydrogen pressure and a zero-order dependence on the hydrocarbon pressures. For both 1-butene and *cis*-2-butene molecules, the hydrogenation rates are insensitive to surface structures. The isomerization rate, however, is doubled for *cis*-2-butene molecules on the stepped platinum surface (Pt(755)).

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1. INTRODUCTION

A catalytic reaction is defined as structure-sensitive if the reaction rate and/or selectivity change significantly on catalysts of different structures. In order to study the structure sensitivity of catalytic reactions, single-crystal surfaces can be employed as model catalysts. Different single-crystal surfaces can be prepared, in order to investigate the chemical activity and selectivity as a function of surface atomic structures and/or different densities of surface defects (steps and kinks).

Platinum is a superior catalyst for a variety of hydrocarbon conversion reactions (1). In suitable reaction conditions (reactant composition, pressure, and reaction temperature), platinum is active for hydrogenation, isomerization, dehydrogenation, dehydrocyclization, and hydrogenolysis reactions. In the previous studies, a surface structure sensitivity has been reported for aromatization, alkane isomer-

ization, and hydrogenolysis reactions at ~600 K on platinum (2). Different surface structures are optimal for different reactions: while a Pt(111) surface yields a faster aromatization reaction than Pt(100), the alkane isomerization rate is 4–7 times higher on Pt(100) than on Pt(111) (2). For some other reactions, the catalytic reaction rate is correlated with the surface irregularities. For example, the increasing number of steps on platinum surfaces increases the aromatization rate while having little impact on alkane isomerization.

The focus of this study is butene hydrogenation and isomerization reactions on platinum surfaces at 300–350 K. Both butene hydrogenation and isomerization reactions are facile at room temperature on supported platinum catalysts (3). In this paper, we discuss the hydrogenation and isomerization reactions of 1-butene and *cis*-2-butene on platinum foil and single-crystal platinum surfaces of (111), (100), and (755) orientation. While the hydrogenation rates are independent of the platinum surface structure, we report a promotion of *cis*-2-butene isomerization reactions on a stepped platinum surface (Pt(755)). The butene isomerization reaction mechanisms are inferred from the reaction products and the catalyst structure sensitivity.

2. EXPERIMENTAL

The experiments were carried out in an ultrahigh vacuum (UHV) chamber which is connected to a high-pressure reaction cell. The UHV system was pumped by a 300 L/s ion pump and a 330 L/s turbomolecular pump. The base pressure in the system was 1×10^{-9} Torr. The apparatus was equipped with an ion sputtering gun, an Auger electron spectrometer (AES), and a quadrupole mass spectrometer. In the UHV chamber, the sample was heated by a 2.0 keV electron beam and the sample temperature was monitored by a chromel–alumel thermocouple pressed to the edge of the sample by a stainless steel weight. The platinum samples (Pt foil, Pt(111), Pt(100), Pt(755)) were mounted on a sample car, with an exposed surface area of $0.6 \text{ cm} \times 0.6 \text{ cm}$. The samples were cleaned by ion bombardment in 5×10^{-5} Torr of neon at room temperature for 10 min, followed by

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annealing in 5×10^{-7} Torr of O_2 at 700 K for 1 min. The cleaning cycle was repeated until no surface contamination (carbon, oxygen, sulfur, etc.) was detected by AES.

The clean samples were then transferred in vacuum to the reaction cell by a transfer rod. The catalytic reaction cell was also connected to a gas manifold, a gas recirculation pump, and a gas chromatography sampling valve. The total volume of the reaction cell is 64 mL. In catalytic reactivity studies, the reaction cell was isolated from the UHV system and filled with ambient pressure reaction mixtures. The catalytic reactions were carried out in a batch mode. The reaction mixtures were analyzed on-line by a gas chromatograph (Hewlett-Packard 3880) with a $30 \text{ m} \times 0.53 \text{ mm}$ GS-alumina capillary column (J & W Scientific). The retention time and FID sensitivity factors of hydrocarbons in the gas chromatograph were calibrated based on an analysis of a standard gas mixture prepared by Scott Specialty Gases. Reaction rates were determined from the product accumulation curves between 10 and 30% conversion of the reactants. The reaction rate data were reproducible within 5%. Blank experiments in the absence of platinum surfaces indicate that the background catalytic reactivity accounts for no more than 3% of the reaction rate.

After completion of the reaction, the reactor was first evacuated to below 10^{-7} Torr by the turbomolecular pump before a gate valve between the reactor and UHV chamber was opened. The sample was then transferred back into the UHV chamber, and the surface contaminants (carbon, oxygen, etc.) were quantified by AES.

Ethylene (Aldrich, 99.5%), propylene (Aldrich 99+%), 1-butene (Aldrich, 99+%), *cis*-2-butene (Aldrich, 95%), isobutene (Aldrich, 99%), and hydrogen (Airco, 99.9995%) were used without further purification. The purity of the hydrocarbon gases was checked by gas chromatography.

3. RESULTS

In the absence of hydrogen, single-crystal platinum surfaces are catalytically inactive for butene reactions. This is significantly different from the supported catalysts, which exhibit reactivity toward alkene isomerization in the absence of hydrogen (4).

In the presence of hydrogen, both hydrogenation and isomerization of 1-butene and *cis*-2-butene are observed on single-crystal surfaces near room temperature. The experiments are conducted on four platinum samples: a polycrystalline Pt foil and single-crystal Pt(100), Pt(111), and Pt(755) surfaces. The Pt(100) surface has a square unit cell, the Pt(111) surface has a close-packed hexagonal structure, and the Pt(755) surface has Pt(111) terraces with average width of six atoms separated by monatomic steps of (100) orientation.

A representative time evolution of reaction products is shown in Fig. 1. On all four platinum surfaces, hydrogenation

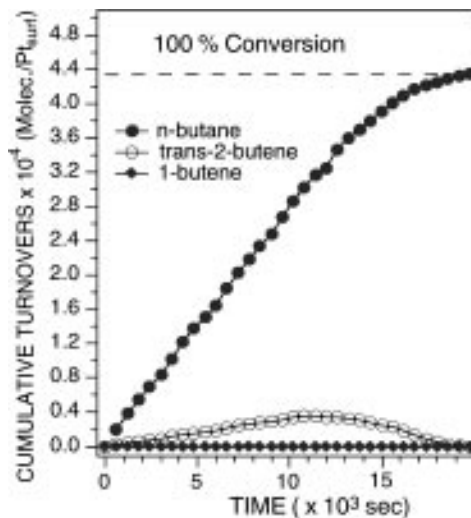


FIG. 1. Accumulative yield of hydrogenation (butane) and isomerization (*trans*-2-butene) products of *cis*-2-butene on Pt(111) at 300 K. The reaction mixture is composed of 7 Torr of *cis*-2-butene and 35 Torr of H_2 .

tion is the major reaction pathway for both 1-butene and *cis*-2-butene molecules. As shown in Fig. 1, the hydrogenation product yield increases steadily to a complete conversion of *cis*-2-butene to *n*-butane. The butene isomerization products, on the other hand, are accumulated only at the initial stage of the reaction before being hydrogenated to *n*-butane. For both molecules under investigation (1-butene and *cis*-2-butene), it is the scenario on all the platinum surfaces.

At room temperature (300 K), the platinum surfaces exhibit a high resistance to deactivation. The time scale of the catalyst deactivation is studied by conducting consecutive reaction studies without any sample cleaning between adjacent runs. After five consecutive runs at room temperature, the platinum catalyst reactivity is lowered by less than 20%, while the ratio of isomerization to hydrogenation rates remains constant. The catalyst deactivation is accelerated at higher reaction temperatures. At a temperature of 350 K, the catalyst reactivity decreases by >70% after a single reaction.

The results of hydrogenation and isomerization reactions are summarized in Sections 3.1 and 3.2, respectively.

3.1. Hydrogenation of 1-Butene and *cis*-2-Butene on Platinum

We first discuss the results of butene hydrogenation reaction. The issues of interest include kinetics of hydrogenation reactions, reaction activation energies and dependence of hydrogenation rates on the platinum surface structure.

The results of 1-butene and *cis*-2-butene hydrogenation reactions are summarized in Table 1. The reaction rates are determined from the accumulative butane (product) yields

TABLE 1

1-Butene and *cis*-2-Butene Hydrogenation on Platinum Surfaces

	Pt foil	Pt(111)	Pt(100)	Pt(755)
1-Butene				
Kinetic order				
Hydrocarbon	-0.1	-0.1	—	-0.2
Hydrogen	1.2	1.2	—	1.0
Activation energy (kcal/mol)	7.9	9.5	10.3	8.9
<i>cis</i>-2-Butene				
Kinetic order				
Hydrocarbon	—	-0.1	—	-0.2
Hydrogen	—	1.1	—	1.0
Activation energy (kcal/mol)	—	10.3	—	9.8

between 10 and 30% conversion of the butene (reactant) molecules. For both butene molecules, the hydrogenation rate is very similar on all of the platinum surfaces, and no structure sensitivity of the hydrogenation rate is detected. Under all the reaction conditions, the platinum surfaces are resistant to deactivation in a time period of hours.

The kinetic orders of the hydrogenation rates are determined by monitoring the reaction rate variation as a function of hydrogen and hydrocarbon pressures. The hydrogen pressure is varied between 7 and 500 Torr, while the butene pressure is changed between 3.5 and 70 Torr. For both 1-butene and *cis*-2-butene molecules, the hydrogenation rates are almost independent of butene pressure but increase linearly with hydrogen pressure. It indicates a near-first-order dependence of the hydrogenation rate on the hydrogen pressure and a zero-order dependence on the hydrocarbon pressure.

The reaction activation energy is determined from the temperature dependence of the hydrogenation rate. Figure 2 displays a representative Arrhenius plot of 1-butene hydrogenation rate on Pt(111). In our studies, the measured activation energy of the hydrogenation reaction ranges from 8 to 10 kcal/mol for 1-butene and *cis*-2-butenes on the platinum surfaces. The small variation in the activation energy data obtained on different platinum surfaces can probably be attributed to the experimental uncertainty.

The butene hydrogenation rates can be compared with other alkene hydrogenation reactions on Pt(111) in order to understand the dependence of alkene hydrogenation reactions on the alkene chain lengths and structures. Figure 3 presents the room temperature (300 K) accumulative hydrogenation product yields for ethylene, propylene, 1-butene, *cis*-2-butene, and isobutene molecules, with 7 Torr of alkene and 70 Torr of hydrogen in the initial reaction mixture. The reaction rate uncertainty is less than 5% for each of the measurements.

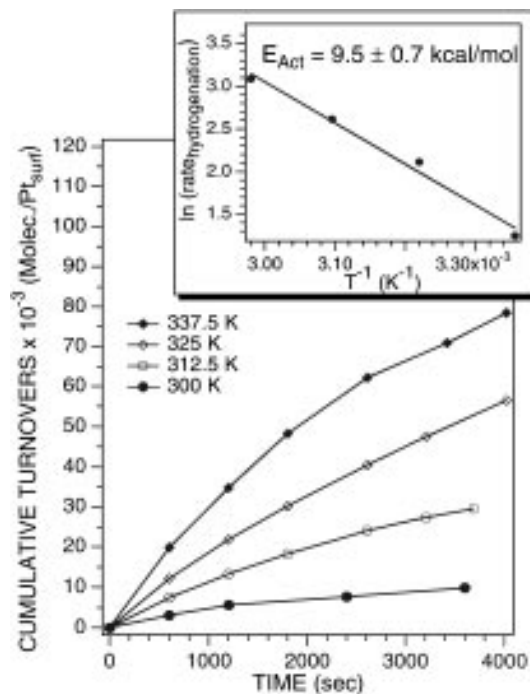


FIG. 2. Accumulative hydrogenation yield of 1-butene on Pt(111) as a function of reaction temperature. The reaction mixture contains 7 Torr of 1-butene and 35 Torr of H_2 . Reaction activation energy is extrapolated from the Arrhenius plot presented in the inset.

The hydrogenation reactions of different alkene molecules on Pt(111) are summarized in Table 2. The reaction rate data are obtained in the present work, while the kinetic order and reaction activation energy values are collected from Refs. (5–7). As shown in Fig. 3, the alkene

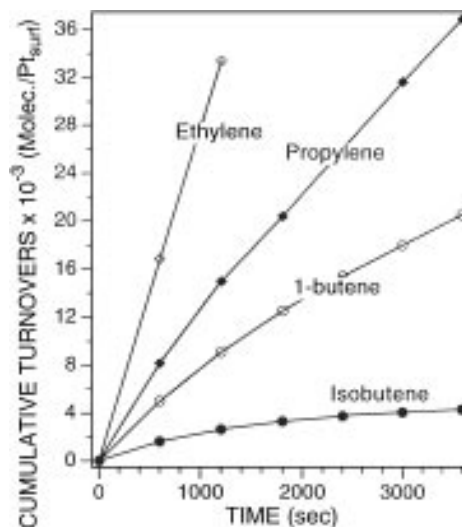


FIG. 3. Accumulative alkene hydrogenation yields on Pt(111) at 300 K. The reaction mixture is composed of 7 Torr of hydrocarbon and 70 Torr of H_2 .

TABLE 2

Comparison of Alkene Hydrogenation Reactions on Pt(111)

Alkene molecule	Kinetic order		Activation energy (kcal/mol)	Reaction rate at 25°C (molecules/Pt · s) ^a
	Hydrocarbon	Hydrogen		
Ethylene ^b	~0	1.0	~10	28 ^d
Propylene ^c	0	0.5	~10	13 ^d
1-Butene ^d	-0.1	1.2	9.5	7
<i>cis</i> -2-Butene ^d	-0.1	1.1	10.3	7
Isobutene ^d	-0.2	0.7	11.8	3 (initial) 0.35 (steady state)

^a 7 Torr hydrocarbon and 70 Torr hydrogen.

^b Reference 5.

^c References 6 and 7.

^d Present work.

hydrogenation rate decreases with increasing carbon chain length. Under the same reaction condition, the hydrogenation rate decreases by ~50% from ethylene to propylene, and another factor of 2 from propylene to 1-butene. The hydrogenation rate is also sensitive to the alkene molecule structure: while similar hydrogenation rates were observed for 1-butene and *cis*-2-butene molecules, a significantly different hydrogenation rate was observed for isobutene molecules on the platinum surface. At room temperature, the hydrogenation rates of 1-butene and *cis*-2-butene decrease by less than 30% on a time scale of hours. By contrast, the isobutene hydrogenation rate is lowered by a factor of ~10 in a short period of time (5–10 min). Although the initial isobutene hydrogenation rate is about half of that of *n*-butene, the steady-state hydrogenation rate of isobutene is more than 1 order of magnitude slower (8).

In a previous work, isobutene hydrogenation on Pt(111) has been investigated by sum frequency generation (SFG) measurements (9). The surface species are tertiary-butyl groups, which are formed by the terminal addition of hydrogen atoms onto the C=C double bonds. The small steady-state turnover rate was attributed to the high stability of tertiary-butyl groups on the platinum surface.

3.2. Isomerization of 1-Butene and *cis*-2-Butene on Platinum

Comparing with competing hydrogenation reaction, isomerization of 1-butene and *cis*-2-butene molecules is the minor reaction channel on the platinum surfaces. As shown in Fig. 1, the butene molecules formed in the isomerization reactions are eventually hydrogenated to butane. As a result, we calculated the isomerization rates based on the data at the initial stage of the reactions, with a conversion of the precursor butene molecules less than 30%.

Table 3 summarizes the results of butene isomerizations at room temperature. The isomerization rates are 5–20% of the hydrogenation rates. At a given temperature, the

ratio of isomerization to hydrogenation rates is very reproducible, with an uncertainty of <1%.

In the presence of hydrogen, 1-butene isomerization yields both *cis*- and *trans*-2-butenes. By contrast, *cis*-2-butene is converted only to *trans*-2-butene on the platinum surface, while 1-butene formation is absent. The results are in good agreement with previous reports on supported platinum catalysts (3).

The structure sensitivity of 1-butene and *cis*-2-butene isomerization is investigated by comparing the reaction rates on different platinum surfaces. 1-Butene isomerization is independent of the platinum surface structure. As shown in Table 3, at the same temperature, the ratio of isomerization rate to hydrogenation rate is comparable on all four platinum surfaces (Pt foil, Pt(111), Pt(100), and Pt(755)). In addition, the isomerization reaction product (*cis*-2-butene and *trans*-2-butene) distribution is similar on all of the surfaces.

Different from 1-butene isomerization reaction, the isomerization of *cis*-2-butene molecules exhibits a significant structure sensitivity. At room temperature, the ratio of isomerization rate to hydrogenation rate is ~9% on Pt foil, ~9% on Pt(111), ~9% on Pt(100), but ~20% on Pt(755). The structure sensitivity exists across the entire reaction temperature range of 300–350 K. Notice that Pt(755) is a Pt(111) surface with a high density of monoatomic steps of (100) orientation, our results suggest that the *cis*-2-butene isomerization is independent of the packing of surface atoms, yet sensitive to the density of line defects on the surface. The competing *cis*-2-butene hydrogenation, however, is independent of the platinum surface structure, regardless of the atomic structure and defect density on the surface (Section 3.1). The different structure sensitivity suggests that *cis*-2-butene isomerization and hydrogenation reactions have different reaction mechanisms. The difference will be discussed later in detail in Section 4.2.

For both 1-butene and *cis*-2-butene molecules, the ratio of isomerization rate to hydrogenation rate is constant regardless of hydrogen (7–500 Torr) and butene (3.5–70 Torr) pressures. It indicates that the isomerization reactions exhibit the same reaction kinetics as the hydrogenation reactions, with a first-order dependence on the hydrogen

TABLE 3

1-Butene and *cis*-2-Butene Isomerization on Platinum Surfaces at 300 K

	Pt foil	Pt(111)	Pt(100)	Pt(755)
1-Butene				
Isomerization/hydrogenation	0.05	0.05	0.05	0.05
<i>trans</i> -2-Butene/ <i>cis</i> -2-butene	0.61	0.55	0.50	0.60
<i>cis</i> -2-Butene				
Isomerization/hydrogenation	0.09	0.09	0.09	0.18
1-Butene/ <i>trans</i> -2-butene	0	0	0	0

pressure and a zero-order dependence on the butene pressure.

The activation energy of butene isomerization reactions is determined from the temperature dependence of isomerization rates, which is ~ 13 kcal/mol for both 1-butene and *cis*-2-butene molecules. The activation energy is significantly higher than that of the hydrogenation reaction (~ 10 kcal/mol). The activation energy difference is evident from the different temperature dependence of isomerization and hydrogenation product yields. For instance, on the Pt(100) surface, the ratio of *cis*-2-butene isomerization to hydrogenation increases from 0.09 at 300 K to 0.30 at 350 K, and the ratio of 1-butene isomerization to hydrogenation increases from 0.05 at 300 K to 0.15 at 350 K. Consistent with a previous study of butene isomerizations on supported platinum catalyst (3), the results suggest that hydrogenation and isomerization reactions do not share the same rate determining step.

The isomerization product distribution is also a function of reaction temperature. 1-Butene is isomerized to both *trans*- and *cis*-2-butene molecules. The relative yield of isomerization products varies as a function of temperature, with the *trans*- to *cis*-2-butene ratio increases from 0.5–0.6 at 300 K to 0.9–1.0 at 350 K. The data indicate that the activation energy for *trans*-2-butene formation is ~ 2.5 kcal/mol higher than that for *cis*-2-butene production.

4. DISCUSSIONS

The butene hydrogenation and isomerization products provide some insight into the reaction mechanisms. First of all, neither isobutene nor isobutane is formed in the reactions of *n*-butene (1-butene and *cis*-2-butene) molecules on platinum between 300 and 350 K. It indicates that C–C bonds remain intact and the surface reaction scheme involves only C–H bond dissociation/formation reactions. It is worth noticing that at high surface temperatures (~ 600 K), platinum is active toward C–C bond cleavage and carbon backbone rearrangement, which lead to hydrocarbon isomerization, dehydrogenation, dehydrocyclization, and hydrogenolysis reactions (1).

4.1. Hydrogenation Reaction Mechanisms

There is evidence from SFG studies that alkene molecules are hydrogenated on platinum by surface hydrogen atoms, which are formed by molecular hydrogen dissociation on the surface (10). Surface-bound alkyl groups (ethyl, propyl, butyl, etc.) are the reaction intermediates after the first hydrogen addition to alkene molecules. An interesting aspect is the regioselectivity in the alkyl group formation, i.e., the position selectivity of H addition to two carbon atoms in the C=C double bond. The two carbon atoms in the C=C double bond are equivalent in 2-butene molecules, and a hydrogen addition is expected to form 2-butyl groups.

In 1-butene molecules, the two carbon atoms in the C=C double bond are inequivalent. A hydrogen atom addition to the internal (2°) carbon atom produces 1-butyl groups, while a terminal addition yields 2-butyl groups.

The regioselectivity issue has been addressed in a recent sum frequency generation (SFG) study of propylene hydrogenation on a Pt(111) surface (11). Under catalytic reaction conditions, the 2-propyl group is the dominant surface intermediate, which can be attributed to a terminal addition of hydrogen to propylene molecules on the surface (11).

There has also been extensive studies on the regioselectivity of hydrogen atom addition onto unsaturated alkene molecules in the gas and condensed phases (12–15). Moore *et al.* examined hydrogen atom addition to propylene and 1-butene at 300 and 573 K (16, 17). Their results indicate that hydrogen atoms add predominately, if not exclusively, to the less-substituted carbon atom of the C=C double bond. Isopropyl and 2-butyl radicals are the dominant products in H atom addition to propylene and 1-butene molecules, respectively. The reaction of hydrogen atoms with olefin thin films condensed below 100 K was investigated by Klein and Scheer (14, 15). Similar to the gas phase results, H atoms add selectively to the terminal carbon atom in propylene and 1-butene molecules. Studies have also been carried out recently on a direct reaction of D atoms with monolayer 1-butene and 1-pentene molecules adsorbed on a Cu(100) surface (18). The predominate reaction pathway is 2-alkyl group formation by a D atom addition to terminal carbon atoms.

Based on the conclusions drawn from these relevant studies, we assume that the terminal addition dominates in the catalytic hydrogen atom addition to 1-butene molecules on the platinum surface, and 2-butyl groups are the surface intermediates in the 1-butene hydrogenation reaction.

4.2. Isomerization Reaction Mechanisms

There are at least two possible mechanisms for catalytic isomerization of butene molecules on metal surfaces.

In the first mechanism, the isomerization reaction is initiated by hydrogenation of butene molecules to form surface alkyl intermediates. The alkyl groups then forfeit a β -H to yield the isomerization products (9, 11).

The second possible reaction mechanism involves dehydrogenation of precursor butene molecules on the platinum surface. The precursor butene molecules first undergo a hydrogen elimination reaction, followed by a hydrogen addition to produce the isomerization products. The mechanism is supported by a dissociative adsorption of butene molecules on platinum (20, 21). This is also the postulated mechanism for butene isomerization on cobalt (19).

On the basis of our experimental results, we believe that surface alkyl groups are likely the reaction intermediates in both hydrogenation and isomerization of 1-butene molecules. However, the hydrogenation and isomerization

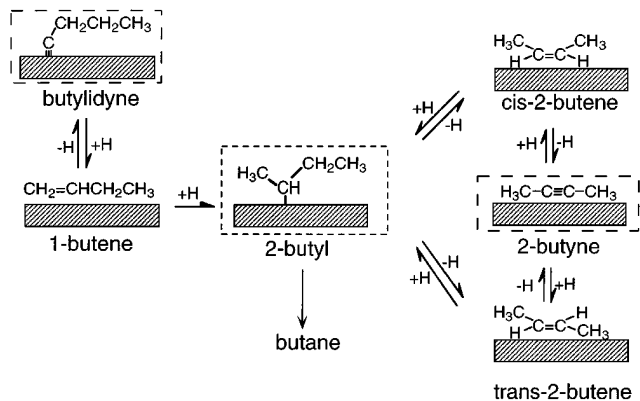


FIG. 4. Proposed mechanism for 1-butene and 2-butene hydrogenation and isomerization reactions.

reactions of *cis*-2-butene molecules do not necessarily share the same surface alkyl intermediates. Instead, the *cis*-2-butene isomerization reaction occurs, at least in part, via the second reaction mechanism, in which it is initiated by a dehydrogenation of precursor butene molecules. The proposed mechanism for the butene isomerization reactions on platinum is presented in Fig. 4.

The reaction mechanism of 1-butene isomerization can be interpreted readily. The decomposition product of 1-butene molecules on the surface is butylidyne ($\text{CH}_3\text{CH}_2\text{CH}_2\text{C}\equiv$) (20, 21), which cannot be transformed directly to 2-butene molecules. Therefore, 1-butene isomerization to 2-butenes must involve a surface 2-butyl intermediate, which is also the transient species in the hydrogenation reaction. This assertion is supported by the fact that both 1-butene hydrogenation and isomerization rates are insensitive to the platinum surface structure.

In contrast to that of 1-butene molecules, the picture is vague for *cis*-2-butene isomerization on the platinum surfaces. The two reaction mechanisms presented at the beginning of this section cannot be distinguished only on the basis of the identity of *cis*-2-butene isomerization products, i.e., *trans*-2-butene but not 1-butene is formed in the isomerization reaction.

As illustrated above, the first mechanism involves a hydrogenation of butene molecules to surface-bound butyl groups, followed by a dehydrogenation of surface butyl groups to butene. This mechanism is supported by some evidence. First, 2-butyl groups are the anticipated surface species formed in a hydrogen atom addition to *cis*-2-butene. Secondly, a hydrogen elimination of 2-butyl groups preferentially yields 2-butene molecules (22). The combination of these two factors can account for the observation that *trans*-2-butene is the sole isomerization product of *cis*-2-butene.

In the second proposed mechanism, the *cis*-2-butene isomerization reaction is initiated by a dehydrogenation of butene molecules, followed by a rehydrogenation to isomerization products. This mechanism is supported by the

fact that *cis*-2-butene molecules decompose into but-2-yne on platinum surface (20). Formation and subsequent hydrogenation of but-2-yne can also justify the absence of 1-butene in *cis*-2-butene isomerization.

Although the two reaction mechanisms can both rationalize the identity of *cis*-2-butene isomerization reactions, only the second mechanism can explain the structure dependence of the butene isomerization reactions.

The first piece of evidence arises from the yields of *trans*-2-butene, which is a common isomerization product for both 1-butene and *cis*-2-butene molecules. As shown in Table 3, there is a notable difference in *trans*-2-butene yield from *cis*-2-butene and 1-butene molecules. This suggests that either *cis*-2-butene and 1-butene isomerizations have different reaction intermediates or that the coverage of the surface intermediates is different for the two reaction systems. Since 2-butyl groups are the proposed intermediates for both 1-butene and *cis*-2-butene hydrogenation reactions, the similar hydrogenation rates suggests a similar coverage of surface 2-alkyl groups for 1-butene and *cis*-2-butene reactions. Since 2-butyl groups are also the proposed surface intermediates for 1-butene isomerization reaction, different isomerization rates for 1-butene and *cis*-2-butene molecules (as gauged by the yield of the common reaction product of *trans*-2-butene) implies that 2-butyl group is not the exclusive surface intermediate in the *cis*-2-butene isomerization reactions.

Another evidence is the unique structure sensitivity of *cis*-2-butene isomerization. On the stepped platinum surface (Pt(755)), *cis*-2-butene isomerization is twice as fast as the reactions on the flat surfaces (Pt(100), Pt(111)). By contrast, 1-butene isomerization and the hydrogenation of both 1-butene and *cis*-2-butene molecules exhibit no sensitivity on the platinum surface structure. The results suggest that the reaction intermediate is different for *cis*-2-butene isomerization and hydrogenation reactions. In addition, the surface intermediate is also different between *cis*-2-butene and 1-butene isomerizations.

In conclusion, the assumption that surface alkyl groups are *cis*-2-butene isomerization intermediate can not justify the difference in the *trans*-2-butene yield between 1-butene and 2-butene reactions. The hypothesis is also inconsistent with the observation that *cis*-2-butene and 1-butene isomerizations exhibit different structure sensitivities. As a result, we postulate that *cis*-2-butene isomerization involves a butene dehydrogenation step. The promotion of *cis*-2-butene isomerization on Pt(755) can be attributed to a facile dehydrogenation of precursor butene molecules at surface line defects.

5. SUMMARY

We studied the competing hydrogenation and isomerization of 1-butene and *cis*-2-butene molecules on platinum at

300–350 K. Both hydrogenation and isomerization reaction rates are first-order in hydrogen and zero-order in butene pressure. At room temperature, the isomerization rate for *n*-butene molecules is 5–20% of the hydrogenation rate on the platinum surface. The ratio of isomerization rate to hydrogenation rate increases with increasing temperature, due to the activation energies of 13 and ~10 kcal/mol for isomerization and hydrogenation reactions, respectively.

Butene hydrogenation rates are compared with the data of ethylene, propylene, and isobutene hydrogenations. On the platinum surfaces, the alkene hydrogenation rate decreases with increasing carbon chain length.

1-Butene isomerization reaction yields both *cis*- and *trans*-2-butene molecules. At the same time, *trans*-2-butene is the only isomerization product for *cis*-2-butene molecules. A significant structure sensitivity is observed for the *cis*-2-butene isomerization reaction, with the reaction rate increases by a factor of 2 on the stepped platinum surface (Pt(755)). No structure sensitivity is detected for 1-butene isomerization as well as hydrogenation reactions for both 1-butene and *cis*-2-butene molecules.

The reaction products, reaction yields and structure sensitivities are indicative of the mechanisms of the surface catalytic reactions. Although 1-butene hydrogenation and isomerization reactions share the same surface reaction intermediate of 2-alkyl groups, the results of our study suggest different reaction mechanisms for *cis*-2-butene hydrogenation and isomerization reactions. At least some of the *cis*-2-butene isomerization reactions involves a C–H bond cleavage to yield but-2-yne, which is subsequently hydrogenated to *trans*-2-butene.

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REFERENCES

1. Somorjai, G. A., in "Introduction to Surface Chemistry and Catalysis." Wiley, New York, 1994.
2. Somorjai, G. A., in "Proceedings, 8th International Congress on Catalysis, Berlin, 1984." Dechema, Frankfurt-am-Main, 1984.
3. Bond, G. C., Phillipson, J. J., Wells, P. B., and Winterbottom, J. M., *Trans. Faraday Soc.* **60**, 1847 (1964).
4. Wells, P. B., and Wilson, G. R., *J. Catal.* **9**, 70 (1967).
5. Zaera, F., and Somorjai, G. A., *J. Am. Chem. Soc.* **106**, 2288 (1984).
6. Otero-Schipper, P., Wachter, W., Butt, J., Birwell, R., and Cohen, J., *J. Catal.* **50**, 494 (1977).
7. Lok, L., Gaidai, N., and Kiperman, S., *Kinet. Katal.* **32**, 1406 (1991).
8. Rogers, G. B., Lih, M. M., and Hougen, O. A., *AIChE. J.* **12**, 369 (1966).
9. Cremer, P. S., Su, X., Shen, Y. R., and Somorjai, G. A., *Faraday Trans.* [Submitted]
10. Horiuti, I., and Polanyi, M., *Trans. Faraday Soc.* **30**, 1164 (1934).
11. Cremer, P. S., Su, X., Shen, Y. R., and Somorjai, G. A., *J. Phys. Chem.* **100**, 16302 (1996).
12. Cvetanović, R. J., *Adv. Photochem.* **1**, 115 (1963).
13. Falconer, W. E., and Sunder, W. A., *Int. J. Chem. Kinet.* **3**, 395 (1971).
14. Klein, R., and Scheer, M. D., *J. Phys. Chem.* **62**, 1011 (1958).
15. Klein, R., Scheer, M. D., and Waller, J. G., *J. Phys. Chem.* **64**, 1247 (1960).
16. Moore, W. J., and Wall, L. A., *J. Chem. Phys.* **17**, 1325 (1949).
17. Moore, W. J., *J. Chem. Phys.* **16**, 916 (1948).
18. Yang, M. X., Teplyakov, A. V., and Bent, B. E., *J. Phys. Chem.*, in press.
19. Phillipson, J. J., and Wells, P. B., *Proc. Chem. Soc.*, 222 (1964).
20. Chesters, M. A., Cruz, C. D. L., Gardner, P., McCash, E. M., Pudney, P., Shahid, G., and Sheppard, N., *J. Chem. Soc., Faraday Trans.* **86**, 2757 (1990).
21. Koestner, R. J., Frost, J. C., Stair, P. C., Van Hove, M. A., and Somorjai, G. A., *Surf. Sci.* **116**, 85 (1982).
22. Teplyakov, A. V., and Bent, B. E., *J. Am. Chem. Soc.* **117**, 10076 (1995).