Hydrogenation of 1,3-butadiene on platinum surfaces of different structures *

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1,3-butadiene hydrogenation is studied on platinum foil and Pt(111), Pt(100), Pt(755) single-crystal surfaces at 300–375 K. The results are compared with the data of alkene hydrogenation reactions. Similar to the hydrogenation kinetics of butenes, 1,3-butadiene hydrogenation exhibits near zeroth-order dependence on hydrocarbon and near first-order dependence on hydrogen pressure. With the same hydrocarbon (3.5–70 Torr) and hydrogen (14–140 Torr) pressure, the rate of 1,3-butadiene hydrogenation is one order of magnitude lower than for the rates for *n*-butenes. The hydrogenation products include 1-butene, trans- and cis-2-butene, and *n*-butane. The reaction selectivity is independent of reactant mixture and platinum surface structure, but changes slightly as a function of reaction temperature. The butene product distribution is determined by surface reaction kinetics. While 1-butene is thermodynamically less stable than trans- and cis-2-butene, it is the major butene product in 1,3-butadiene hydrogenation.

Keywords: hydrogenation, isomerization, 1,3-butadiene, platinum

1. Introduction

Recently, hydrogenation and isomerization reactions of 1-butene and cis-2-butene were studied on platinum foil and Pt(111), Pt(100) and Pt(755) single-crystal surfaces [1]. In the temperature range of 300–350 K, with a hydrogen pressure between 7 and 500 Torr and a butene pressure of 3.5–70 Torr, hydrogenation is the predominant reaction pathway. While 1-butene hydrogenation kinetics is insensitive to platinum surface structure, cis-2-butene isomerization is accelerated by a factor of two on a stepped Pt(755) surface.

In this paper, we examine 1,3-butadiene hydrogenation reaction on platinum in the temperature range of 300–375 K. The reaction rate and selectivity are studied on a number of well-defined platinum surfaces: Pt(111), Pt(100), Pt(755) single-crystal surfaces and a platinum foil. 1,3-butadiene hydrogenation products include butane and a number of butene isomers. Our main objective is to monitor the reaction selectivity as a function of hydrocarbon pressure, hydrogen pressure, surface temperature and platinum surface structure.

1,3-butadiene hydrogenation was previously studied on platinum catalysts of other forms. On supported platinum catalysts, 1,3-butadiene hydrogenation was carried out at a temperature range of 275–425 K [2]. The kinetic order of hydrogenation is 1.3 with respect to hydrogen and −0.5 with respect to 1,3-butadiene. With increasing temperature, the selectivity toward butenes increases, along with the ratio of cis-2-butene to trans-2-butene. In a follow-up study, the reactivity of platinum wires was examined [3]. At a temperature of 400–600 K, butenes are the major reaction products, while near equal amount of trans-2-butene and cis-2-butene are formed.

2. Experimental

The experiments were carried out in an ultra-high vacuum (UHV) system in connection with a high-pressure reaction cell. The ultra-high vacuum 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 UHV system was equipped with an ion sputtering gun, an Auger electron spectrometer 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. The platinum samples (Pt foil,

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Pt(111), Pt(100), Pt(755)) were mounted on a sample car, with an exposed surface area of 0.6 cm × 0.6 cm. The samples were cleaned by ion bombardment in 5×10^{-5} Torr neon at room temperature for 10 min, followed by annealing in 5×10^{-7} Torr O_2 at 700 K for 1 min. The cleaning cycle was repeated until no surface contamination was detected by Auger electron spectroscopy (AES). The clean samples were then transferred in vacuum to the reaction cell by a transfer rod. The catalytic reactor is connected to a gas recirculation pump and a gas chromatography sampling valve, with a total volume of 64 ml. In catalytic reactivity studies, the reaction cell was isolated from the UHV vacuum system and filled with ambient pressure reaction mixtures. The reaction was carried out in the batch mode, and reaction mixtures were analyzed by an on-line gas chromatograph (Hewlett-Packard 3880) equipped with a 30 m × 0.53 mm GS-alumina capillary column (J&W Scientific). The retention times 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 increase of product accumulative yields as a function of time, and the results 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 total reactivity. After completion of the reaction, the reactor was first evacuated to below 10–7 Torr by a turbomolecular pump, the gate valve between the reactor and UHV chamber was then opened, the sample was transferred back into the UHV chamber, and the post-reaction surface was characterized by AES.

1,3-butadiene (99+%) and hydrogen (Airco, 99.9995%) were used without further purification. The purity of the hydrocarbon gases was checked by gas chromatography.

3. Results

The hydrogenation of 1,3-butadiene was carried out on platinum foil and single-crystal Pt(100), Pt(111) and Pt(755) surfaces between 300 and 375 K. The reaction mixtures are composed of 3.5–70 Torr of 1,3-butadiene and 14–140 Torr of hydrogen. 1,3-butadiene hydrogenation products include *n*-butane, 1-butene, cis-2-butene and trans-2-butene. The reaction kinetics are reported in terms of overall hydrogenation rate and product selectivities. Three reaction selectivities define the product composition: ratio of butene to butane, ratio of 2-butene to 1-butene, and ratio of trans-2-butene to cis-2-butene. Since all the experiments were carried out under identical conditions on clean surfaces, the results provide direct comparison of 1,3-butadiene hydrogenation kinetics on different platinum surfaces.

3.1. 1,3-butadiene hydrogenation rate

Under 7 Torr 1,3-butadiene and 70 Torr hydrogen at 300 K, the hydrogenation rate for 1,3-butadiene is ~ 0.9 molec./(Pt s) on platinum foil. It is about one order of magnitude slower than the hydrogenations of 1-butene and cis-2-butene molecules, which have a turnover number of ~ 9 molec./(Pt-atom s) under the same reaction conditions [1].

A typical accumulation turnover curve for 1,3-butadiene hydrogenation on Pt(111) at 300–350 K is shown in figure 1. As shown in the figure, the reaction rate is

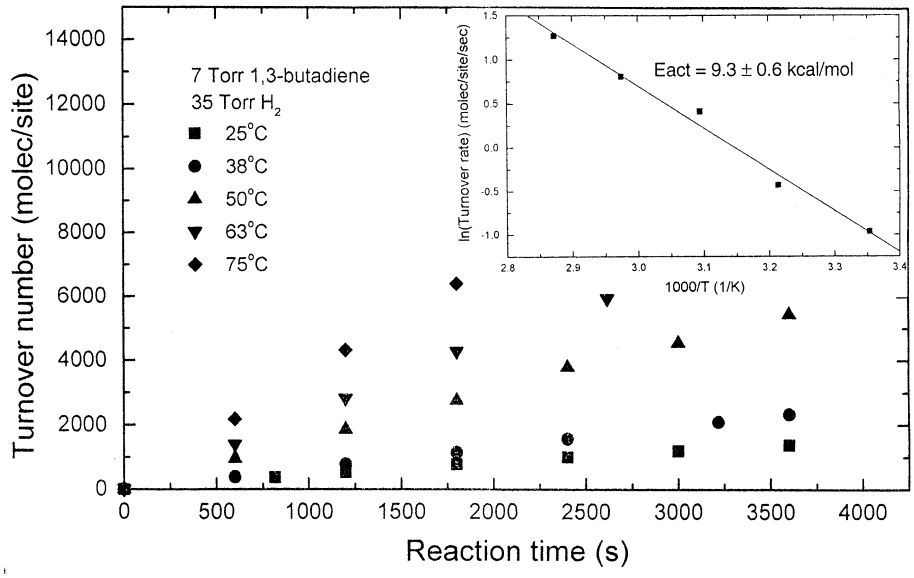

Figure 1. Accumulative turnover numbers for 1,3-butadiene hydrogenation on Pt(111) at 300–350 K. The reaction mixture contains 7 Torr 1-butene and 35 Torr H_2. Activation energy of the reaction is obtained from the Arrhenius plot presented in the inset.

Table 1
Kinetic data of 1,3-butadiene hydrogenation on platinum surfaces

Surface structure	Kinetic order [a]		Activation energy [a] (kcal/mol)	Turnover rate [b] (molec./(Pt s))
	1,3-butadiene	hydrogen		
Pt foil	−0.10	1.16	9.7	0.90
Pt(111)	–	–	9.3	0.85
Pt(100)	–	–	12.7	0.27
Pt(755)	−0.13	1.12	9.7	0.71

[a] At 300–350 K.
[b] 7 Torr of 1,3-butadiene, 70 Torr of hydrogen, and at 300 K.

constant up to 60 min. The platinum foil and single-crystal platinum surfaces are resistant to deactivation. After five consecutive reactions carried out at room temperature, the platinum catalyst reactivity is decreased only by $< 10\%$. In addition, a Pt(111) sample air-exposed for 15 min maintains $> 50\%$ of reactivity.

The kinetic orders of the hydrogenation rate are determined by monitoring the reaction rate change as a function of hydrogen and hydrocarbon pressures. The hydrogen pressure is varied from 14 to 140 Torr, while the butadiene pressure is changed from 3.5 to 70 Torr. As summarized in table 1, the reaction orders are −0.1 and 1.1 with respect to 1,3-butadiene and hydrogen pressures, respectively. The reaction activation energy is determined from the temperature dependence of the hydrogenation rate, as presented in the inset. An error bar of ~ 0.7 kcal/mol is placed on the activation energy data.

The reaction rate and activation energy depend on the catalyst structure. At room temperature, the hydrogenation rate is $\sim 33\%$ smaller on Pt(100) than on other surfaces (Pt(111), Pt(755) and platinum foil). Reaction activation energy is also significantly different on Pt(100) (12.7 kcal/mol) from other surfaces (9.3–9.7 kcal/mol). The activation energy difference is > 3 kcal/mol, well beyond the uncertainty of our measurements (0.7 kcal/mol). As a result, we can conclude with confidence that the activation energy of 1,3-butadiene hydrogenation is sensitive to surface structure. It is worth noticing that an activation energy of 19 kcal/mol was reported for the reaction on supported platinum catalysts [2].

3.2. 1,3-butadiene hydrogenation selectivity

Figure 2 displays a representative time evolution of 1,3-butadiene hydrogenation product distribution on platinum foil at 300 K. The product composition is independent of conversion at the early stage of the reaction. Selectivity toward butenes decreases gradually with reaction time, which can be attributed to a re-adsorption and hydrogenation of butene molecules on the surface in a secondary reaction. In the meantime, however, the

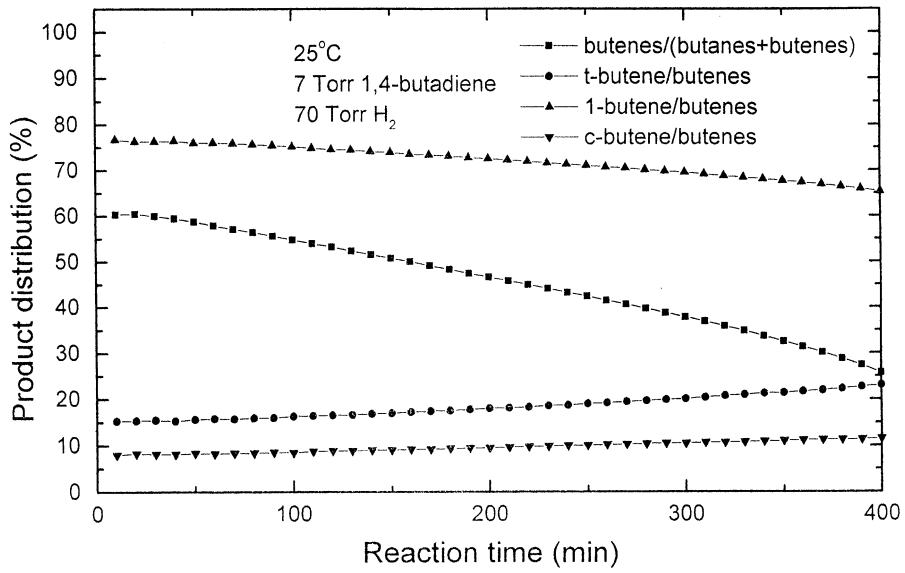

Figure 2. Product composition as a function of reaction time for 1,3-butadiene hydrogenation on platinum foil at 300 K. The reaction mixture is composed of 7 Torr of 1,3-butadiene and 70 Torr of hydrogen.

product distribution of butene isomers remains steady until a complete conversion of 1,3-butadiene molecules.

The reaction selectivity for 1,3-butadiene hydrogenation on platinum surfaces is summarized in table 2. The product distribution is independent of 1,3-butadiene and hydrogen pressures. The product distribution is also irrelevant to platinum surface structure. However, the product composition is dependent upon reaction temperature. On all four platinum samples under investigation, the selectivity to butenes increases with increasing surface temperature. In addition, the ratio of cis-2-butene to trans-2-butene yields increases with surface temperature. While the thermodynamically more stable trans-2-butene is in excess relative to cis-2-butene at room temperature (300 K), near equivalent amounts of trans-2-butene and cis-2-butene are formed in the reaction at 375 K.

The reaction selectivity is also insensitive to surface contamination. While the reaction rate decreases by 50% on an air-exposed Pt(111) surface, the product distribution matches the data collected on a clean surface. The results suggest that the multiple reaction products share the same surface intermediates.

4. Discussion

Surface butenyl groups are the reaction intermediates after the first hydrogen addition to 1,3-butadiene molecules. An interesting aspect is the regioselectivity in the butenyl formation, i.e., the position selectivity of H addition to two carbon atoms in 1,3-butadiene molecules. A hydrogen atom addition to the internal carbon atom produces 1-butenyl ($-CH_2-CH_2-CH=CH_2$). A terminal addition, by contrast, yields 2-butenyl ($-CH(CH_3)CH=CH_2$), which can also be regarded as a methyl-substituted allyl group. The 2-butenyl group is energetically more stable. From a thermodynamic point of view, the terminal addition should be the major reaction pathway.

The regioselectivity can also be anticipated based on the adsorption geometry of 1,3-butadiene molecules on the platinum surface. The adsorption of 1,3-butadiene on Pt(111) was recently studied by near edge X-ray absorption fine structure (NEXAFS) [4]. A di-σ coordination is proposed for 1,3-butadiene chemisorption at 300 K. The configuration is substantiated by high-resolution electron energy loss spectroscopy (HREELS) studies. In the di-σ coordination of 1,3-butadiene, a double bond connects two carbon atoms at the center of the molecule, while two terminal carbon atoms bind directly with substrate atoms. Previous studies suggest that hydrogen addition to a C=C double bond is slower than a hydrogen insertion to a carbon–metal bond. For instance, in alkene hydrogenation reactions, H addition to the C=C bond is the rate-determining step, which is slower than the subsequent reaction of hydrogen with the carbon–metal bond in alkyl groups. In the case of 1,3-butadiene molecules with a di-σ coordination on platinum, a hydrogen insertion to the carbon–metal bond accounts for a terminal addition to 1,3-butadiene molecule.

1,3-butadiene hydrogenation products on platinum include 1-butene, cis- and trans-2-butenes and *n*-butane. Two issues of interest are the selectivity toward butene formation and the distribution of butene isomers.

It is a common agreement that the surface hydrogenation reactions proceed in series from 1,3-butadiene via butene isomers to yield *n*-butane [5]. Although 1,3-butadiene hydrogenation is one order of magnitude slower than butene hydrogenations on the clean surface, a significant amount of butene isomers is formed in the reaction scheme. As shown in table 2, the selectivity toward butene molecules is 0.56–0.67 at 300 K. The results can be justified by a strong chemisorption of 1,3-butadiene on the surface. Our experiments indicate that 1,3-butadiene hydrogenation is near zeroth order with respect to butadiene pressure. It implies that 1,3-butadiene molecules are strongly chemisorbed on platinum surfaces, and the surface coverage of 1,3-butadiene is not in proportion to its gas phase pressure. A strong adsorption of 1,3-butadiene on the surface prevents the readsorption of butene molecules, thus suppresses the further hydrogenation of butene isomers to *n*-butane.

The distribution of butene isomers is also interesting. 1-butene is formed in a 1,2-hydrogen addition to 1,3-butadiene. A competing 1,4-hydrogen addition reaction yields 2-butene isomers. In our studies, the butene isomers are formed in non-equilibrium proportions. 1-butene, the thermodynamically least stable isomer, is the major product of all the reactions. It suggests that 1,2-

Table 2
Product composition for 1,3-butadiene hydrogenation on platinum surfaces [a]

Surface structure	Butenes/(butanes + *n*-butane)		trans-2-butene/cis-2-butene	
	300 K	350 K	300 K	350 K
Pt foil	0.56	0.65	2.78	1.47
Pt(111)	0.67	0.72	2.23	1.26
Pt(100)	0.52	0.75	2.00	1.20
Pt(755)	0.62	0.65	2.23	1.50

[a] 7 Torr of 1,3-butadiene and 70 Torr of hydrogen.

addition is a significant reaction channel in the hydrogenation scheme.

Finally, we report a structure sensitivity of 1,3-butadiene hydrogenation activation energy. Four platinum samples were examined in our studies: Pt(100) has a square unit cell on the surface; Pt(111) surface has a close-packed hexagonal structure; Pt(755) has Pt(111) terraces of an averaged width of six atoms separated by a monatomic Pt(100) step, and amorphous platinum foil is full of surface defects. The surface atomic density is 1.50×10^{15} for Pt(111), 1.47×10^{15} for Pt(755), 1.23×10^{15} for Pt(100) surface, respectively. Our results suggest that 1,3-butadiene hydrogenation is insensitive to the defect density on the surface, but sensitive to the surface structure on the platinum surface. It is apparent that activation energy for 1,3-butadiene hydrogenation is slightly higher on a platinum surface of (100) orientation.

5. Summary

1,3-butadiene hydrogenation reaction was studied on platinum foil and Pt(100), Pt(111), Pt(755) single-crystal surfaces at 300–375 K. Turnover rate for 1,3-butadiene hydrogenation is one order of magnitude smaller than for *n*-butenes. The reaction is near first order with respect to hydrogen pressure, and near zeroth order in 1,3-butadiene pressure. The product composition is constant at the early stage of the reaction, and virtually independent of the platinum surface structure. Raising reaction temperature increases the selectivity toward butene formation, as well as the relative yield of cis-2-butene with respect to trans-2-butene.

At room temperature, 1,3-butadiene hydrogenation rate is similar on Pt(111), Pt(755) single-crystals and Pt foil. However, the reaction is significantly slower on Pt(100). In addition, a reaction activation energy of 12.7 kcal/mol is obtained on Pt(100), which is higher than the activation energy of 9.3–9.7 kcal/mol observed on other platinum surfaces.

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