# Hydrogenolysis and Isomerization of *n*-Butane on Low-Index Pt Single Crystals and Polycrystalline Pt Foil

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The hydrogenolysis and isomerization of *n*-butane over Pt(100) and Pt(111) single crystals and a polycrystalline Pt foil have been studied over a wide range of reaction temperatures (510-610 K) and hydrogen partial pressures (7.5-250 Torr). The activity and selectivity have both been determined as a function of temperature and hydrogen partial pressure. The more open Pt(100) surface was an order of magnitude more active than the close-packed Pt(111) surface. Hydrogenolysis selectivities were invariant with reaction temperature over the range studied. Hydrogen partial pressure affected both the activity and product distribution. Both single-crystal surfaces exhibit a decrease in the activity as the H<sub>2</sub> pressure is decreased below a critical amount and this decrease is directly attributable to the formation of a carbonaceous surface residue. The amount of isomerization was always less than the amount of hydrogenolysis regardless of the *n*-butane to hydrogen ratio or the reaction temperature. (C) 1996 Academic Press, Inc.

# INTRODUCTION

The effect of supported metal morphology on catalytic reactivity has been the topic of a large number of investigations over the past twenty-five years (1–5). Generally, morphology is conventionally varied by changing the size of the metal particles (which in turn affects the coordination of surface atoms and their environment). Metal particle morphology is also thought to be affected by the oxide support, but conclusive evidence is often lacking since particle shapes in supported catalysts are not easy to define unequivocally. More recently, there have been a number of studies where metal particle shapes were varied by annealing particles in different gaseous atmospheres at elevated temperatures (6-8). These experiments were performed on model systems where the metal was evaporated on planar thin films of oxide support such that particle shapes could be unambiguously determined. These model systems, however, are not convenient for reactivity measurement. Hence the precise effect of metal particle shape and morphology on catalytic reactivity continues to be difficult to establish.

We have chosen to work with a different kind of model

catalyst system, one in which three-dimensional particle shapes and the catalytic reactivity of the metal surfaces can both be determined. This is accomplished by using oxide particles with simple geometric shapes as model supports. Nonporous oxide supports have the advantage that the metal particles are located exclusively on the convex surfaces of the oxide particles and therefore can be examined readily by high-resolution transmission electron microscopy. Using these model supports, we have found that large particles of Pt supported on silica exhibited a morphological dependence on the atmosphere in which they had been treated (9). When heated at 923 K in 200 Torr of H<sub>2</sub>, large Pt particles exhibited well-defined cubo-octahedral shapes with prominent (111) surface facets. When the particles were subsequently heated in 70 Torr of  $O_2$ , the particles become much more rounded with the (111) facets being less well defined. This thermally induced restructuring was completely reversible. Studies of the reactivity behavior of these model catalysts of controlled morphology are presently under way in our laboratory. To establish a connection between morphology and reactivity, we have chosen to examine hydrocarbon conversion reactions on these Pt catalysts.

In view of its commercial importance as a catalyst for hydrocarbon conversion reactions, the behavior of Pt catalysts has been intensively studied. Bond (3) has elegantly summarized our current understanding of the variables that control the catalytic behavior of supported Pt (1–3). The study of well-defined single crystals of Pt by Somorjai and co-workers (10-12) provides direct information about the role of surface structure on reactivity of hydrocarbons. One problem encountered when comparing literature data from single-crystal investigations with that from supported catalysts is the large discrepancy in the reaction conditions used. The majority of studies on supported Pt are performed under conditions of flowing gases at atmospheric or higher pressure while single-crystal studies have been carried out in batch reactors, usually at subatmospheric pressures. The reactant pressure, as will be shown, can lead to quite significant differences in catalytic behavior.

The catalytic properties of supported Pt model catalysts are currently being investigated in our laboratory, however, as mentioned above, there is only limited kinetic data available on single-crystal Pt model catalysts with which these results on supported catalyst can be compared. Therefore, as a first step, we have examined the catalytic behavior of Pt(111) and (100) single crystals and polycrystalline Pt foil. The structure-sensitive reaction of isomerization and hydrogenolysis of *n*-butane have been chosen as probe reactions. We have employed a wide range of reaction temperatures and hydrogen partial pressures so that comparisons can be made with the silica-supported Pt catalysts. In a subsequent publication, we will report the reactivity behavior of supported metal catalysts whose morphology has been varied by annealing treatments to gain insight into the role of Pt surface morphology on catalytic behavior.

#### **EXPERIMENTAL**

All reaction experiments and surface analysis were performed in one of two systems. Each was a UHV chamber coupled to a high-pressure reactor via a gate valve. The base pressure for each system was  $2.0 \times 10^{-10}$  Torr. Typical operating pressures were between  $7.0 \times 10^{-10}$  and  $3.0 \times 10^{-9}$ Torr. The first system had the capability for a wide range of surface analysis experiments, including LEED, XPS, AES, inert gas LEISS, and thermal desorption experiments. The second system utilized AES and TPD to monitor surface composition, in addition a variable energy ion gun was available for sample cleaning. Both systems have been described in detail elsewhere (13, 14).

The Pt(100) and Pt(111) single crystals and the polycrystalline foil had an exposed surface area of approximately 1 cm<sup>2</sup>. The crystals were spot welded between two tungsten heating leads that were in turn spot welded to two stainless steel supports. The supports were mounted on the copper feed throughs of a standard UHV sample manipulator. The samples were resistively heated by a DC power supply that was current controlled by a feedback PID controller. Samples could be heated to 1300 K. The crystals and foil were initially cleaned by a series of sputter/oxidize/anneal cycles. The samples were sputtered with 2.5 keV Ar ions at approximately 10–15  $\mu$ A for 20 min with  $T_{Pt} = 873$  K. The samples were then oxidized at 923 K in 5.0 × 10<sup>-7</sup> Torr of O<sub>2</sub>. Following the oxidation, the crystals were then annealed to 1250 K.

The long-range ordering of both crystals has been characterized by LEED and each exhibited a sharp pattern corresponding to its orientation. Carbon monoxide thermal desorption was performed on each of the crystals and the results closely matched literature observations (15, 16). The surface composition was routinely monitored for carbon, oxygen, and impurities such as Si, S, and B diffusing out from the bulk. A typical reaction sequence consisted of cleaning the crystal with an oxidation/anneal cycle, analyzing the surface composition with AES, retracting the crystal into the reactor and performing the analytic reaction, evacuating the reactor, and finally performing post reaction surface analysis.

Reactant gases were research grade *n*-butane (99.9%), UHP H<sub>2</sub> (99.9995%), UHP O<sub>2</sub> (99.9985) from Matheson, and UHP Ar (99.9998%) from Trigas. The *n*-butane was further purified by a set of five freeze/thaw cycles. The H<sub>2</sub> was stored in a glass bulb under liquid nitrogen during use. The main impurities in the *n*-butane feed were ~0.04% propane and ~0.06% iso-butane as measured by gas chromatography. All gas analysis was done with either an HP 5400 or an HP 5890 gas chromatograph equipped with a flame ionization detector. Separations were accomplished with either 6-ft Poropak N or 6-ft 0.19% picric acid on Carbowax packed columns.

#### RESULTS

The number of Pt atoms was assumed to be  $1.505 \times 10^{15}$ /cm<sup>2</sup> for the (111) crystal and  $1.470 \times 10^{15}$ /cm<sup>2</sup> for the (100) crystal. The atom density for the polycrystalline foil was assumed to be  $1.5 \times 10^{15}$  Pt atoms per cm<sup>2</sup>. Activity measurements are reported as a turnover frequency (TOF), i.e., the number of *n*-butane molecules that react per surface Pt atom per second. The TOF was calculated using the following equation:

$$\text{TOF} = \frac{\left[ (P_{nC_4})(V_{\text{rctr}})/RT \right] X_{nC_4} N_A}{\Theta_{\text{s}} t_{\text{rxn}}}$$

where  $\Theta_s$  is the number of surface Pt atoms,  $X_{nC_4}$  is the fractional conversion,  $N_A$  is Avagadro's number,  $t_{rxn}$  is the reaction time in seconds,  $V_{rctr}$  is the reactor volume (liters),  $P_{nC_4}$  is the initial pressure of the *n*-butane in the reactor (Torr), *T* is the temperature (K), and *R* is the ideal gas constant (liter Torr)/(mole K).

In Fig. 1 the activity for the hydrogenolysis and isomerization of *n*-butane over each of the Pt catalysts is shown in Arrhenius form. The reaction conditions were 50.0 Torr  $H_2$  and 0.5 Torr *n*-butane. The activation energies, determined from the least-squares fit of the Arrhenius plots, are  $25.0 \pm 2.9$  and  $27.3 \pm 3.4$  kcal/mole for the (100) and (111) facets, respectively. The activation energies were computed by a least-squares fit to the data. The Pt(100) crystal face is nearly an order of magnitude more active than the Pt(111)face for the hydrogenolysis of *n*-butane, while the polycrystalline Pt was approximately a factor of two more active than the Pt(100) crystal. The TOFs reported here for both crystals differ from those reported by Davis et al. (10), due in part to the different reaction conditions used. Davis et al. used a  $H_2: nC_4$  ratio of 10:1 and a total pressure of 220 Torr while the total pressure used in our study was 50.5 Torr with a  $H_2$ :  $nC_4$  ratio of 100. As will be shown below, the  $H_2$ 



FIG. 1. Arrhenius plot for the hydrogenolysis and isomerization of *n*-butane over Pt(100), Pt(111), and polycrystalline Pt foil.

partial pressure greatly influences the catalytic activity for hydrogenolysis.

The product distributions, as a function of reaction temperature, for both surfaces are shown in Fig. 2. The first salient feature to point out is that over the temperature range studied, neither surface is capable of isomerizing *n*-butane to iso-butane. The hydrogenolysis products do not vary significantly with temperature for either surface. Both surfaces exhibit a high degree of multiple hydrogenolysis, i.e., cleavage of more than one C–C bond in the molecule. The multiple hydrogenolysis is manifested in methane being the dominant product over both surfaces. The amount of ethane formed, from cleavage of the central C–C bond,



FIG. 2. Selectivity of *n*-butane hydrogenolysis and isomerization as a function of reaction temperature over Pt(100) (left panel) and Pt(111) (right panel).



**FIG. 3.** Selectivity of *n*-butane hydrogenolysis and isomerization as a function of hydrogen partial pressure over Pt(100).

remains constant over the temperature range investigated and is approximately equal for the (100) and (111) surfaces. The higher methane production seen on the (100) plane comes at the expense of the propane formation, which is significantly lower over the (100) surface than on the (111)surface. For Pt(111), the average methane to propane ratio is 2.1, while for Pt(100) the ratio is 13.6. Over the temperature range 533 to 575 K, the selectivity of the polycrystalline foil, not shown here, was identical to that of the (100)surface.

The effect of the hydrogen partial pressure on the selectivity for the (100) surface is depicted in Fig. 3. It should be noted here that the total pressure for this set of experiments was held constant at 250.5 Torr and the pressure of the *n*-butane was held at 0.5 Torr. As the H<sub>2</sub> pressure was varied, the balance was made up with argon. Clearly, the extent of isomerization is dependent on the ratio of hydrogen to hydrocarbon. The amount of iso-butane produced gradually increases with decreasing hydrogen partial pressure. Also, as the H<sub>2</sub> to hydrocarbon ratio drops below 25, the rate of ethane formation begins to increase, and at an H<sub>2</sub> pressure of 7.5 Torr, over 30% of the product formed is ethane, while the amount of propane produced falls to zero.

The  $P_{\rm H_2}$  dependence of the product selectivities for Pt(111) is displayed in Fig. 4. Unlike the Pt(100) surface, the extent of *n*-butane isomerization is negligible on Pt(111) and iso-butane initially present as contamination in the *n*-butane feed in fact begins to crack at low hydrogen partial pressures. The negative amount of iso-butane shown at the lowest H<sub>2</sub> pressure is caused by the procedure used to correct for the iso-butane present in the feed, a procedure that is not perfect when dealing with small amounts of iso-butane produced. Multiple hydrogenolysis seems to be subsiding at the low hydrogen pressures as evidenced by

0.6

0.5

0.4

FIG. 4. Selectivity of *n*-butane hydrogenolysis and isomerization as a function of hydrogen partial pressure over Pt(111).

the increased amount of ethane and propane and the lower methane selectivity.

The effect of hydrogen partial pressure on the activity of the Pt(100) is depicted in Fig. 5. Clearly, the activity goes through a maximum over a H<sub>2</sub> pressure range of approximately 50 to 100 Torr which corresponds to hydrogen to *n*-butane ratio between 100 and 200. As the  $H_2$  pressure is increased further the activity drops. Such behavior has been reported in the literature for other Group VIII metals (17). The decrease in the activity at low  $H_2$  pressures is

TOF

C/Pt AES

TOF (nC4 molec. react/Pt atom/sec) C/Pt AES Ratio 0.3 P(nC4) = 0.5 Torr P(tot) = 250.5 Torr 0.2 T(rxn) = 550 K 0.1 0.0 .001 1000 1 10 100 Hydrogen Partial Pressure FIG. 5. Activity for *n*-butane hydrogenolysis and isomerization and corresponding carbon to Pt Auger ratio as a function of hydrogen partial pressure for Pt(100).

FIG. 6. Activity for *n*-butane hydrogenolysis and isomerization and corresponding carbon to Pt Auger ratio as a function of hydrogen partial pressure for Pt(111).

accompanied by the buildup of a carbonaceous residue on the surface of the crystal as was determined by postreaction AES analysis and is shown in Fig. 5. Davis et al. (11) have reported a similar poisoning of Pt surfaces by deposition of a nongraphitic form of carbon. A similar activity pattern is observed for the Pt(111) surface as displayed in Fig. 6. As the hydrogen partial pressure is lowered, a rapid decrease in the activity is seen. Again, the accumulation of carbonaceous deposits on the catalyst surface is evident at low H<sub>2</sub> pressures. The direct comparison of the activity patterns of the two surfaces is not straightforward because of the different total pressure applied on the two surfaces.

Figure 7 demonstrates the deactivation of the Pt(111)surface as a function of reaction time at a given reaction temperature and reactant ratio. The procedure for this experiment was to run the reaction for a given time, analyze the reaction gas mixture with gas chromatography, transfer the catalyst into UHV to measure the C/Pt ratio, and then perform another reaction on the carbon-covered surface without cleaning the crystal. The activity drops by a factor of 10 after a reaction time of 25 min whereas the amount of carbon deposited increases. This deactivation is also seen for both the (100) and polycrystalline Pt samples. For the Pt(100) surface, the deactivated surface is approximately 10% as active as the initially clean surface. It is interesting to analyze the product distribution for each surface as a function of reaction time. Figure 8 shows the change in product selectivity as a function of reaction temperature over the Pt(111) surface. The amount of methane formed on the carbon-covered surface is significantly higher than that on the clean surface, i.e., 60% as opposed to 38%. This increase in methane selectivity comes at the expense of both ethane and propane which are seen to decrease. For the





1

.1



FIG. 7. Activity and carbon to Pt Auger ratio for n-butane hydrogenolysis and isomerization as a function of reaction time for Pt(111).

Pt(100) and polycrystalline surfaces, the selectivities are invariant with the reaction time, and the methane selectivity remains between 60 and 75% for both surfaces.

### DISCUSSION

The results of this study show that the Pt(100) surface is over an order of magnitude more reactive than the Pt(111)surface for the hydrogenolysis of *n*-butane under identical reaction conditions. The polycrystalline Pt foil is about a factor of 2 greater in activity than the Pt(100) surface. The activities reported in the Arrhenius plots are for deactivated surfaces and are not the initial rates. Deactivation was quite rapid, and for example at 575 K, the activity leveled off



**FIG. 8.** Selectivity for *n*-butane hydrogenolysis and isomerization as a function of reaction time for Pt(111).

after about 10 min. No attempt was made to extrapolate back to zero reaction time due to the rapid deactivation at short times and the consequent difficulty of getting a precise estimate of the initial rate. The reaction times varied with temperature, with shorter times being used at higher temperatures so that conversions did not exceed 5%.

The higher reactivity of the (100) surface compared to the (111) surface is similar to that seen for *n*-butane hydrogenolysis on Rh (18) and ethane hydrogenolysis on Ni (19). The higher activity of the (100) surface has been attributed to the more open and atomically rougher surface structure of this crystal face (19). This interpretation is consistent with the observed activity of the polycrystalline foil being even greater than that of Pt(100), since the polycrystalline foil has a larger fraction of surface defects and grain boundaries and therefore a larger number of coordinatively unsaturated surface atoms. One of the most important structural differences between Pt(111) and Pt(100) is the presence of threefold hollow sites on the former surface. It has been shown (20-22) that these threefold hollow sites are capable of forming stable alkylidyne species which are unique to surfaces that have threefold symmetry. If the surface intermediate formed on the (111) surface is much more stable than that formed on the (100) surface a lower activity should be expected for the (111) surface.

Another significant difference between the (111) and (100) surfaces is their ability to bind hydrogen. Any difference in surface hydrogen concentration is important during the hydrogenation of the adsorbed hydrocarbon species after C-C bond cleavage. It has been demonstrated (23, 24) that hydrogen bonds to Pt(100) more strongly than to Pt(111), therefore the (100) surface should have a higher relative coverage of H atoms. Consequently, the hydrogenation of the adsorbed hydrocarbon species is often enhanced on the (100) surface thus resulting in higher hydrogenolysis activities. This is consistent with the data shown on Figs. 5 and 6 where the rollover in reaction order from positive to negative occurs at a lower pressure for the (100) surface. Under our experimental conditions, the rate of reaction on Pt(111) remained positive order even at the highest H<sub>2</sub> pressures investigated. These results for Pt(111) and Pt(100) differ significantly from those of Davis et al. (10), who found that the activity of Pt(100) was nearly the same as that for Pt(111) at 573 K. The discrepancies could be caused, in part, by the differences in reaction conditions applied. The partial pressures of the reactants used in the study of Davis et al. (10) were 10 Torr of *n*-butane and 200 Torr in H<sub>2</sub>, whereas the activities in this study were determined in a gas mixture of 0.5 Torr *n*-butane and 50 Torr H<sub>2</sub>.

Also associated with the different surfaces are changes in their respective product distributions. The polycrystalline and (100) surfaces of Pt exhibit a higher degree of multiple hydrogenolysis, manifested in the high methane selectivity, than does the (111) plane of Pt. The general trends in product selectivities are in accord with product distributions observed for the Rh(111) and Rh(100) (18) surfaces and for the Ir(111) and Ir(110) (25) surfaces. Clearly, the selectivity for alkane hydrogenolysis is sensitive to the morphology of the catalyst surface. The selectivities are invariant with temperature over the range studied, as might be expected for catalysts that exhibit significant multiple hydrogenolysis reactions.

The selectivities observed in our study are in marked contrast to those reported by Davis et al. (10), who found that Pt(111) exhibited a statistical distribution (i.e., one third each of methane, ethane, and propane) of hydrogenolysis products while Pt(100) yielded 60% ethane and equal amounts of methane and propane. In addition to differences in hydrogenolysis selectivity, Davis (10) reported that both the (100) and (111) surfaces yielded more isomerization products than hydrogenolysis products. For all conditions used in our study, the selectivity toward hydrogenolysis far exceeded that of isomerization. In fact, even at the lowest reaction temperature studied, the amount of methane formed was greater than what would be expected from a statistical distribution. The relative temperature invariance of the product distribution indicates that the mechanistic pathway is not changing over the temperature range investigated. It has been suggested (30) that the *n*-butane adsorbs through the 1,2-carbon atoms and this leads to the preferential cleavage of the terminal C-C bonds. Breaking of the terminal bond will yield  $CH_x$  and  $C_3H_y$  surface species. The  $C_3H_v$  can undergo further cleavage to yield  $C_2H_z$  and  $CH_a$  or it can be hydrogenated off from the surface to form propane. Our product distribution results suggest that the predominant pathway for ethane formation is the C-C bond cleavage of the adsorbed  $C_3H_{\nu}$  fragments.

The very high isomerization selectivities reported by Davis et al. (10) are somewhat surprising since the great majority of studies of *n*-butane and hydrogen on Pt report significantly less isomerization than hydrogenolysis. Several other research groups that have studied the reaction of *n*-butane and hydrogen (on supported Pt and oriented Pt films) report significantly less isomerization activity, where in fact the hydrogenolysis activity is always greater than the isomerization activity (26–29). For *n*-butane plus H<sub>2</sub> on an oriented Pt(100) film, Anderson and Avery (26) report an isomerization selectivity of 16% at 573 K and H<sub>2</sub>:*n*C<sub>4</sub> of 12. The same group reports an isomerization selectivity of 12% on a Pt(111) oriented film at a reaction temperature of 593 K. Their investigation of *n*-butane isomerization on an unoriented Pt film yield 11% selectivity at 553 K.

Dowie *et al.* (27) also report isomerization selectivities which are less than hydrogenolysis selectivities for unoriented Pt films. Their isomerization selectivity values range from 8 to 44% depending on the reaction conditions. Two other groups (28, 29) studying the reaction of *n*-butane and hydrogen on supported Pt also report that hydrogenolysis is the dominant reaction pathway when compared to isomerization. The reason for the high isomerization selectivity reported by Davis *et al.* (10) is not clear from analysis of results reported here or in the literature.

Hydrogenolysis and isomerization of *n*-butane were performed on the Pt(100) surface at 575 K and 20 Torr on *n*-butane and 200 Torr of hydrogen. Again, the selectivity towards hydrogenolysis far exceeded that of isomerization. Under these conditions 18% iso-butane was formed, with the hydrogenolysis selectivity for methane, ethane, and propane equal to 52, 21, and 9%, respectively.

A comparison of the product distributions for the (100) and (111) surfaces reveal both differences and similarities between the two surfaces. Both surfaces exhibit a preference for methane production and both produce approximately equal amounts of ethane. Besides the striking similarity of producing about the same amount of ethane  $(\sim 25\%)$  its selectivity is independent of the temperature, over the range studied. This could be explained by the possibility that the ethane is produced on defect sites such as edge or corner atoms. Both crystals were approximately  $1 \text{ cm}^2$  per side and 1 mm thick. This would suggest that the number of defect atoms would be nearly the same, which then would imply that the Pt atoms on both (100) and (111) surfaces cleave terminal C-C bonds preferentially. Differences between the surfaces manifest themselves in the amount of  $C_3H_{\nu}$  that is hydrogenated off the surface to form propane. On the (100) surface practically all of the  $C_3H_{\nu}$  species undergo further C–C bond cleavage to form exclusively methane. On the (111) surface a portion of the  $C_3H_{\nu}$  is hydrogenated off to form propane and the remainder undergoes hydrogenolysis to produce methane and ethane. The implication here is that the  $C_3H_{\nu}$  species is more strongly adsorbed to the Pt(100) surface than to the (111) surface.

Low-energy electron diffraction was used to determine that the crystals were highly ordered, therefore one cannot attribute the different product distributions to imperfections in these crystals. We therefore conclude that the different selectivities in the earlier study by Davis *et al.* (10) must be attributed in part to the different partial pressures or differences in methods used to correct for the background concentration of iso-butane in the *n*-butane feed.

The experimental determination of the hydrogen partial pressure dependence is not straightforward since the rapid deactivation at low H<sub>2</sub> partial pressures makes it difficult to obtain reliable reaction rates. However, it is clear that the low activity at low partial pressures of H<sub>2</sub> is caused by large amounts of carbon that are deposited on the surfaces at low H<sub>2</sub>/*n*-butane ratios. This is different from what is seen for either Ir (25) or Rh (18). For Ir it has been shown that as the H<sub>2</sub> pressure decreases, the activity levels off but does not drop (25). This has been ascribed to a change in the rate-limiting step from C–C bond cleavage to desorption of the hydrogenolysis products. At H<sub>2</sub>:  $nC_4$  ratios greater than

150, the rate can be expressed as the competitive adsorption of H<sub>2</sub> and *n*-butane with the cleavage of C-C bonds being the rate-limiting step. This has also been reported to be the case for *n*-butane hydrogenolysis over Ir single crystals, but for  $H_2: nC_4$  ratios greater than 20. The decrease in the concentration of surface hydrogen is regarded to be responsible for this change in rate limiting step. On Pt surfaces, it appears that the carbon deposited at low  $H_2/n$ -butane ratios acts to block or modify the available reaction sites. For Pt(111), not only is the amount of surface carbon at low  $H_2$ pressures causing a decrease in activity but it changes the product distribution as well. One possible explanation for this observation is that the carbon preferentially blocks the sites where internal C-C bond cleavage takes place, thus yielding the higher methane concentration. A second possibility is that the surface carbon is being hydrogenated and desorbing as methane. This change in selectivity is not seen on either the Pt(100) or polycrystalline Pt surface, where the amount of methane is already high.

As seen from Fig. 5, there is a maximum in activity with increasing H<sub>2</sub> pressure, and such a maximum has also been reported to occur over supported Pt/silica catalysts (3, 29). Competition between the parent hydrocarbon and H<sub>2</sub> for surface sites leads to a drop in activity at high H<sub>2</sub> pressures. Comparison of Figs. 5 and 6 shows that the TOF begins to roll over at a higher hydrogen pressure for the Pt(111)surface than for the Pt(100) surface. This clearly supports the evidence that the (100) surface has a higher concentration of hydrogen than the close-packed (111) surface, at an equivalent temperature. Both surfaces exhibit a loss in activity as a function of reaction time, for a given temperature. This loss in activity correlates well with a increase in the amount of carbon on the surface. In addition to the change in activity, in Pt(111) surface also shows a change in selectivity with the more deactivated surface producing an increased amount of methane. What is not clear yet is whether the increased rate of methane formation is a result of the hydrogenation of the accumulated surface carbon or an enhancement in the terminal bond scission pathway relative to the internal bond scission pathway.

Two important aspects have emerged from this study, the first is that neither Pt(100) or (111) are capable of the isomerization of *n*-butane to iso-butane under the experimental conditions of this study. The second aspect is that differences in hydrogenolysis activities and selectivities exist between the two crystal faces and these differences are significant enough to help in the study of supported Pt catalysts with known particle morphology. The aim of this study has been to establish the effect of temperature and H<sub>2</sub> partial pressure on the catalytic behavior of unsupported, well-defined Pt surfaces for the reaction of *n*-butane and hydrogen. These results will be used to elucidate the effect of particle microstructure on the reaction of *n*-butane and H<sub>2</sub> for silica supported Pt catalysts.

## CONCLUSIONS

The activities and selectivities for the hydrogenolysis and isomerization of *n*-butane have been measured for polycrystalline Pt and Pt(100) and Pt(111) single crystals. The experiments were performed over wide ranges of reaction temperatures and  $H_2$  partial pressures. The open (100) surface was approximately an order of magnitude more active than the close-packed (111) surface, in accordance with what has been reported for Rh and Ni single crystals. Product distributions for the single crystals were different in that the (100) face had a higher methane selectivity, indicating more multiple hydrogenolysis. Neither surface produced substantial amounts of iso-butane, as the quantity of hydrogenolysis products was always much higher than that of isomerization. Both single-crystal surfaces show considerable deactivation at low H<sub>2</sub> pressures due to carbon deposition, with slight changes in the selectivity at low H<sub>2</sub> pressures. Also, both surfaces demonstrate a loss in activity as a function of reaction time and concomitantly there is an increase in the amount of carbon on the surface. These results will be used to provide a baseline for determining the effect of supported particle microstructure for a silica-supported Pt catalyst where the morphology can be controlled by thermal treatment in different gaseous atmospheres.

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