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The Hydrogenolysis and Isomerization of Light Hydrocarbons Over Pt Catalysts

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Abstract

There is evidence that metallic Pt, unlike Ni and Rh, has the ability to isomerize light hydrocarbons in the presence of hydrogen. The nature of the active site for the isomerization is still unclear though. It has been shown that the morphology of a silica supported Pt particles can be controlled by heating in different atmospheres and that annealing in hydrogen produces cubo-octahedral particles. The reaction of n-butane with H₂ was carried out over two silica supported Pt catalysts of different particle sizes and a Pt(111) single crystal. Comparison of the product distribution between the two supported and the single crystal sample are the focus of this paper.

Introduction

For many commercial applications, ranging from petroleum refining to the production of fine chemicals, isomerization of a specific hydrocarbon molecule is an important step in the overall process. One impediment to this isomerization pathway is the destruction of the parent molecule through hydrogenolysis. It was found that Pt supported on alumina was capable of isomerizing hydrocarbons through a bifunctional pathway where the Pt acted as the adsorption and dehydrogenation site and the alumina acid sites isomerized the hydrocarbon¹. This reaction pathway competes directly with the hydrogenolysis of the parent hydrocarbon. It was later shown that addition of Sn, to form a bimetallic catalyst, reduced the ability of the Pt/alumina to crack hydrocarbon molecules². It has also been postulated that Pt, without the aid of acidic sites, is capable of isomerizing hydrocarbons³. Much less work has centered on the nature of monofunctional Pt as an isomerization catalyst and how the product distribution of a hydrocarbon reaction is affected by the nature of the active Pt sites is still unclear.

In order to investigate the intrinsic isomerization ability of metallic Pt, we have reacted n-butane with hydrogen over silica supported Pt and a unsupported Pt(111) single crystal. Transmission electron microscopy (TEM) provides evidence that upon annealing silica supported Pt particles in H₂ they exhibit a cubo-octahedral shape with a high density of (111) planes.⁴ Thus, we are able to control the morphology of the Pt particles and make direct comparisons with the single crystal results.

Experimental

Reaction studies for the supported catalysts were performed in a differential quartz flow reactor with a Type K thermocouple inserted directly in the catalyst bed. The respective flow rates for H₂ and n-butane were 20 std. cm³/min (sccm) and 1.0 sccm at a total pressure of ~640 Torr. The support used for the large particle catalyst was model silica spheres prepared by a sol-gel technique⁵. For the small particle sample, Grace silica gel was employed. The first sample was prepared by wet impregnation H₂PtCl₆ and had an average particle diameter, as determined by TEM, was 150Å with a nominal weight loading of 5.0%. The second sample, prepared by ion-exchange of Pt(NH₃)₄(NO)₂, had a nominal weight loading of 1.0% and an average particle diameter of less than 40Å. Single crystal experiments were performed in a batch reaction cell

coupled to a UHV analysis chamber where post reaction surface analysis was carried out. In all cases, the n-butane contains approximately 0.08% iso-butane. This was subtracted out for each run.

Results and Discussion

Shown below, in Figure 1, is a plot of the hydrocarbon selectivity for n-butane plus H_2 on the Pt(111) plane as a function of temperature. As can be seen, the selectivity is invariant with temperature at these respective partial pressures, with methane the dominant product and i-butane always less than 10% of the total product. For statistical cleavage, a one to one ratio of methane to propane would be seen. If the parent molecule cleaves more than once while adsorbed on the surface this would manifest itself in an increased amount of methane in the final product distribution and this is precisely what is seen. It should be pointed out that at temperatures above 610 K, significant amounts of dehydrogenated products are formed. In Fig. 1 no attempt was made to separate the ethylene from ethane or the propane from propylene. At 610 K, the ethylene was approximately one third the amount of ethane with the propylene being roughly 25% of the propane.

The next step was to determine the dependence of the product distribution on the partial pressure of hydrogen. This is shown below in Fig. 2. Again, the amount of iso-butane formed is always less than any of the other products and at H_2 pressures below 10 Torr the iso-butane in the feed begins to crack. At partial pressures above 25 Torr, which corresponds to a n-butane to H_2 ratio of 50 to 1 the selectivity is relatively independent of the H_2 pressure. Multiple hydrogenolysis is seen in the increased amount of methane formed relative to propane, i.e. a ratio of methane to propane greater than one. The appearance of dehydrogenated products is seen at H_2 pressures below 20 Torr. The apparent reaction order for H_2 is 0.8 between hydrogen pressures of 17 and 100 Torr.

Figure 1.
Selectivity as a Function of Temperature for the n-Butane Plus Hydrogen on a Pt(111) Single Crystal

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Figure 2.
Selectivity as a Function of Hydrogen Partial Pressure for
n-Butane Plus Hydrogen on a Pt(111) Single Crystal

A similar experiment was performed where the total pressure was varied at a constant hydrogen to hydrocarbon ratio of 100 to 1.0. As previously shown for hydrogen partial pressure dependence, the selectivity towards isomerization was less than that for hydrogenolysis and methane was the predominant product. In fact, a plot of the selectivity as a function of total pressure closely resembles the selectivity as a function of hydrogen partial pressure as is seen in Fig. 3.

Figure 3.
Selectivity as a Function of Total Pressure for n-Butane Plus Hydrogen on a Pt (111) Single
Crystal

A comparison of what was known to occur on a (111) single crystal was made to silica supported Pt particles, of two different average particle diameters. Shown below, in Fig. 4, are the selectivities for the two supported catalysts at a reaction temperature of 648 K. There are two noticeable differences in the product distribution of the two catalysts. The first is that the small particles produce much more iso-butane than do the large particles. Second, the hydrogenolysis products are nearly statistically distributed for the catalyst with the 40Å particles, while the large

particles exhibit a strong tendency towards multiple hydrogenolysis. In fact, the large particles have a product distribution that is almost identical to that of the Pt(111) single crystal. The selectivities for both supported samples were independent of the reaction temperature over the range 598 K to 648 K. On a per gram Pt basis, the 40Å catalyst was roughly a factor of 3 times more active than the large particle catalyst. It should be noted that when the hydrogen to hydrocarbon ratio is less than ten to one, the catalyst deactivates rapidly and is not regenerable unless oxidized. This is seen in a drop in activity and a corresponding increase in the carbon content on the surface as determined by Auger electron spectroscopy.

It has been shown that well defined Pt (111) planes, whether supported or unsupported, are not capable of isomerization of n-butane to iso-butane under conditions of excess hydrogen. The 40Å particles did show a significant amount of isomerization. This could very well be due to the fact that for Group VIII elements, as the particle size decreases the number of coordinatively unsaturated atoms increases, and it is possible that these atoms contribute to the make up of the active isomerization site⁶. The next step in this project is to determine how different crystal faces affect the product distribution and make comparisons with a wider range of supported particle sizes.

Figure 4.
Comparison of Selectivities for n-Butane Plus Hydrogen on Two Silica Supported Pt Catalysts with Different Particle Sizes

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