Oxidative Restructuring of Rhodium Metal Surfaces: Correlations between Single **Crystals and Small Metal Particles**

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The influence of oxidation on the activity and selectivity of rhodium for n-pentane hydrogenolysis has been studied. The catalytic behavior of Rh(100) and Rh(111) single crystals was contrasted with that of a 2 wt % Rh/SiO₂ supported catalyst to elucidate the role of the support. It was found that the activation energy for hydrogenolysis and the product distribution were significantly different on Rh(111) and Rh(100). The product distribution and activity of the annealed (773 K in H₂) Rh/SiO₂ catalyst matched very well the behavior of the Rh(111) single crystal. Oxidation of the Rh(111) single-crystal surface as well as the Rh/SiO₂ catalyst at 773 K and $P_{O_2} = 70$ Torr led to an enhancement in activity, a change in activation energy, and hydrogenolysis selectivity. No surface oxygen could be detected by Auger electron spectroscopy (AES) on the oxidized single-crystal metal surface after reaction, suggesting that the reactivity changes were associated with differences in morphology. Oxidation of rhodium leads to an apparent "roughening" of the metal surfaces that persists under reaction conditions. The roughening is manifested by multiple cleavage of C-C bonds within the *n*-pentane molecule at temperatures where the annealed surfaces cleave a single C-C bond during hydrogenolysis.

Introduction

Preoxidation of supported metal catalysts is known to result in altered reactivity.¹⁻⁴ These reactivity changes could be caused by subsurface oxygen, altered morphology of the metal particles, and/or could represent an influence of the support. An understanding of the mechanisms underlying this phenomenon is important since oxidizing pretreatments are often used to regenerate catalysts in industrial practice. The chemistry of the metal oxide formed on Rh has recently been studied by high-resolution TEM, EXAFS, LEED, XPS, and TPD.⁵⁻⁹ The resulting oxide does, under certain circumstances, grow epitaxially on the metal surface,^{7,10} however, the stoichiometry and structure of the oxide depend on the oxidation conditions.^{5,7}

One of the consequences of oxidation is an increase in volume due to the lower density of the oxide.¹¹ The subsequent reduction conditions control the atom mobility and thereby determine the resulting surface structure. When the reduction is done at low temperatures, it is possible that the surface is restructured and leads to altered activity and selectivity in the oxidized-reduced catalyst. One possible mechanism for such restructuring is the breakup of large (>100 nm) particles into smaller (<10 nm) particles as observed on silica supports.¹ The silica support was assumed to facilitate this breakup by providing a surface on which the metal would spread during oxidation. More recently,³ these reactivity changes due to oxidation and reduction were found to occur without any particle breakup. In this work, we have compared the activity of single crystals and supported metal particles subjected to identical oxidizing pretreatment in order to better understand the role of the support during oxidation-reduction cycling

Hydrogenolysis reactions are known to be sensitive to structure¹² and provide an excellent probe for studying the metal surface. There have been numerous studies¹³⁻¹⁵ of hydrocarbon hydrogenolysis over supported rhodium. Yates and Sinfelt¹³ found that the ethane hydrogenolysis activity of Rh/SiO₂ supported catalysts reached a maximum at a particle diameter of ≈ 50 Å. In the hydrogenolysis of *n*-pentane, Yao et al.¹⁴ observed a dramatic change in product distribution with increasing metal loading of Rh supported on alumina. Yacaman et al.¹⁵ suggested that changes in product distribution could be related to the structure of the metal particles: icosahedral vs cubooctahedral. The catalysts they studied, however, contained both types of particles, making it difficult to derive a simple correlation between structure and reactivity. The observed changes in activity and selectivity

We find that the hydrogenolysis activity and selectivity of annealed Rh(100) differ considerably from those of annealed Rh(111) in agreement with the known structure sensitivity of this reaction. The catalytic behavior of ca. 5 nm Rh particles supported on silica, after annealing at high temperatures in hydrogen, is modeled quite well by the annealed Rh(111) single crystal. Oxidative pretreatments cause pronounced changes in the activity and selectivity for *n*-pentane hydrogenolysis on both the single crystals and the supported catalyst. The absence of surface oxygen after reaction, as determined by AES, confirms that the reactivity changes are due to altered morphology that is stable under reaction conditions.

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should be related not to the bulk structure of the metal but to its surface structure which can be accomplished by using single crystals of the metal in known orientations. Hence, in this paper, we have measured the reactivity of Rh(111) and Rh(100) single crystals and compared the catalytic behavior with that of supported Rh using *n*-pentane hydrogenolysis as a test reaction. We chose to work with these single-crystal orientations because the (111) and (100) were the only well-defined facets seen in previous studies of supported Rh metal particles.⁵ The comparison of single crystals and supported metal particles provides a better understanding of the surface structure of small metal particles and intrinsic (volume-driven) versus extrinsic (support-mediated) effects during oxidative pretreatment of Rh.

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Experimental Section

An ultra-high-vacuum (UHV) surface analysis chamber was constructed with a vacuum interlocked microcatalytic highpressure reactor.¹⁶ The ultimate pressure obtainable in both sections was less than 1×10^{-10} Torr, using a Thermionics 220 L/s ion pump. The surface analysis chamber was equipped with a PHI 10-155 single-pass cylindrical mirror analyzer [for Auger electron spectroscopy (AES)], a UTI-100C quadrupole mass analyzer [for temperature-programmed desorption (TPD)], a Rh metal evaporator, and a gas microdoser attached to an UHV ion-pumped (thermionics 20 L/s) gas handling system. Crystals were mounted on a retraction bellows and translated vertically between the analysis chamber and the reaction chamber. The reaction chamber could be independently evacuated with a 50 L/s Leybold Heraeus turbomolecular pump (TMP). The rhodium-(111) crystal was 1 mm thick, 10 mm square, and was polished to within $1/2^{\circ}$ of the (111) face while the rhodium(100) single crystal was 1 mm thick and had a 10 mm diameter and was polished to within $1/2^{\circ}$ of the (100) face. The rear face of the crystal was spot welded to 0.50-mm W (AESAR 99.98%) wire leads and to a chromel/alumel thermocouple. The manipulator included both power and chromel/alumel thermocouple feedthroughs which allowed heating from 296 to 1373 K.

The Rh single crystals were cleaned by oxidation (oxygen 99.997%, Matheson) at 1000 K and 3×10^{-8} Torr for 10 min followed by a 30-s vacuum anneal at 1100 K until all impurities were removed. The same cleaning procedure was used before oxidation of the Rh single crystal at higher pressures in the reaction chamber. HPLC grade *n*-pentane (99.0%) was obtained from Fisher Scientific and was further purified by multiple distillation to remove ethane, propane, and *n*-butane impurities. The final purity of the pentane was 99.7% with the impurities being isopentane and neopentane. Further purification was not attempted since the hydrogenolysis of the pentane isomers is much slower at these reaction temperatures and the total amounts of these isomers remained constant during reaction. Hydrogen (99.9995%) was supplied by Matheson and used without further purification.

Hydrogenolysis reactions were generally carried out at a pressure of 210 Torr with a 20:1 hydrogen:*n*-pentane ratio. After reaction, a 50-cm³ sample was expanded into an evacuated stainless steel sample cylinder and allowed to equilibriate for 1 h. This sample was then injected into a Varian 3400 gas chromatograph and the products analyzed with a flame ionization detector. After reaction, the gas-phase products were pumped off with the TMP and the crystal translated into the surface-analysis chamber to monitor surface carbon and oxygen after reaction. The crystal was flashed to 573 K before analysis by AES to remove weakly bound species. The AES spectra were collected with a 2-V peak-to-peak modulation.

Supported catalysts were prepared by impregnation of rhodium(III) 2,4-pentanedionate on silica spheres. The catalysts were dried in air at 383 K and then reduced in H₂ at 473 K overnight. Reactions were carried out in a quartz batch reactor using conditions identical with those used for the single crystals, i.e., a total pressure of 210 Torr with a 20:1 hydrogen:*n*-pentane ratio. The number of exposed Rh atoms was determined by static volumetric chemisorption of H₂ in the pressure range 0–100 Torr by using the experimental setup described previously.⁵ The chemisorption stoichiometry was assumed to be H/Rh = 1. Hydrogenolysis reactivity was expressed as a turnover frequency (TOF) in units of molecules of *n*-pentane converted per surface Rh atom per second.

Results

Hydrogenolysis Reactivity over Rh Single Crystals. The turnover frequencies for *n*-pentane hydrogenolysis $(H_2/n-C_5 = 20/1)$ on the Rh(100) and Rh(111) single crystals before and after oxidation are plotted in Figure 1 in an Arrhenius plot. The activation energy for *n*-pentane hydrogenolysis on Rh(100) is 22 kcal/mol while



Figure 1. Reactivity of Rh(111) and Rh(100) single crystals for *n*-pentane hydrogenolysis in the annealed state and after preoxidation in 70 Torr at 773 K. The activity of the preoxidized surfaces is not corrected for any surface area increase caused by the oxidative restructuring.



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Figure 2. AES spectrum for Rh(100) single crystal (A) clean and (B) after reaction using 200 Torr of hydrogen and 10 Torr of *n*-pentane.

on Rh(111) it is 47 kcal/mol. Since the Rh crystals were supported with W leads which are normally slightly hotter than the crystal, we also checked the background reactivity of a polycrystalline W (AESAR 99.95%) foil. The W foil was treated in the same manner as the Rh single crystals using similar leads and was found to be completely unreactive (4 orders of magnitude lower) at the reaction conditions used for the Rh crystals.

The surface composition of the metal was studied by Auger electron spectroscopy (AES). Figure 2 presents spectra for the clean Rh(100) surface and after the crystal was used for *n*-pentane hydrogenolysis. The large peak is the Rh 302-eV transition and the only impurities detected after reaction were submonolayer amounts of carbon (272 eV) and a trace of Cl (181 eV). Since the carbon peak in the AES spectrum lies between the major Rh transitions, it is difficult to quantify the carbon surface coverage.¹⁷

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Figure 3. Hydrocarbon product distribution for the *n*-pentane hydrogenolysis reaction on the annealed single crystals of (a, top) Rh(111) and (b, bottom) Rh(100).

The amount of surface carbon did not change significantly over the range of temperatures reported in Figure 1. The reaction rate measured after surface analysis (without flashing), and with no further cleaning, was identical with that on the clean surface within experimental error. This surface carbon could be readily reacted to CH_4 upon heating in H_2 , confirming that it was carbidic in nature.

When the cleaned Rh(100) single crystal was heated in 50 Torr of H₂ at 673 K, a larger Cl peak was detected by AES than normally seen after the hydrogenolysis reaction runs. Since no Cl peak was seen on the Rh(111) crystal after a similar H_2 treatment, we suspect that the Cl impurity was diffusing from the bulk of the Rh(100) crystal. We also found that the hydrogenolysis reaction rate on the H2-treated Cl-covered Rh(100) surface was identical with that on the clean Rh(100) surface. In fact, the Cl peak observed on the H2-treated Rh(100) surface diminished in size after the hydrogenolysis reaction was performed, indicating that it was probably reacted away by H₂ under reaction conditions. In general, we were unable to correlate the trace amount of CI on the surface after reaction with any changes in hydrogenolysis reactivity. The AES spectra on the Rh(111) surface were similar to those on Rh(100) discussed above with the exception that no Cl peak was detected after reaction.

The selectivity of the *n*-pentane hydrogenolysis as a function of temperature for both the Rh(111) and Rh(100) surfaces is presented in Figure 3. On the clean metal surfaces, the product distribution was consistent with scission of a single C-C bond from *n*-pentane at low temperatures. Under these conditions, the amount of methane formed was approximately equal to that of *n*-butane and likewise the amount of propane formed was equal to that of ethane. At higher temperatures, multiple cleavage of C-C bonds in *n*-pentane occurs and the fraction of methane in the products starts to increase. The temperature where the





Figure 4. AES spectrum for the Rh(100) single crystal after (A) oxidation in 70 Torr of O_2 at 795 K and (B) after performing *n*-pentane hydrogenolysis on the preoxidized single-crystal surface.



Figure 5. Surface oxygen concentration on Rh(100) after oxidation for 10 min in 1 Torr and 70 Torr of O_2 . (The error limits are ± 0.025 units on the ordinate.)

transition from single to multiple hydrogenolysis occurs is indicated by the dotted vertical line. The Rh(111) single crystal shows a much higher selectivity to ethane and propane than the Rh(100) surface over the range of temperatures corresponding to single hydrogenolysis of the *n*-pentane.

The partial pressure dependence of the *n*-pentane hydrogenolysis activity was also studied on the Rh(100) and Rh(111) singlecrystal surfaces (T = 473 K). The hydrogen order appears to be +0.5 when the pressure is increased from 20 to 200 Torr and nearly zero order above this pressure on both the single-crystal surfaces. The reaction rate was nearly zero order in *n*-pentane pressure over the range investigated (2-100 Torr). Selectivities for the reaction remained constant within experimental error during these runs.

Nature of the Oxide Formed on Rhodium Single Crystals. Figure 4 shows an AES spectrum from the Rh(100) surface after oxidation in 70 Torr of O_2 at 795 K and after being used for *n*-pentane hydrogenolysis in 200 Torr of H_2 and 10 Torr of *n*-pentane. It can be seen that no surface oxygen is present (within the limits of detection by AES) after reaction and that the carbon deposited during reaction is also comparable to that seen in Figure 2b. The



Figure 6. Desorption of oxygen (32 amu) from preoxidized Rh(100) during temperature-programmed desorption at 10 K/s.

extent of oxidation of the Rh(100) surface was studied as a function of temperature both at 1 Torr and at 70 Torr of O_2 . Figure 5 shows the relative atom fraction of O on the Rh(100)surface calculated by using sensitivity factors $(S_{\rm Rh}/S_{\rm O} = 1.5)$ and the equations reported in the PHI handbook.¹⁸ Similar results for the Rh(111) surface are reported elsewhere.⁷ Since we are dealing with a thin film of oxide it is undoubtedly difficult to derive the true stoichiometry by AES. What we are reporting is an average stoichiometry within the information depth of the AES technique. The maximum atomic concentration of O attained on the Rh(100) surface corresponds to a stoichiometry of $Rh_2O_{2.6}$. In 1 Torr of O_2 , this stoichiometry was attained at a temperature of 790 K, but at 70 Torr this stoichiometry could be achieved even at 630 K. In previous work⁷ on Rh(111), we also found that the maximum surface atomic O concentration corresponded to an average stoichiometry of $Rh_2O_{2.6}$. Increasing oxidation time (up to 10 h) in 70 Torr of O_2 and \approx 790 K did not alter the average stoichiometry of the oxide, suggesting that oxide films deeper than the AES information depth are being formed under these conditions. Temperature-programmed desorption of O₂ in Figure 6 also suggests that a thicker oxide film is being formed at 1 Torr of O_2 and 782 K than at lower temperatures. As will be shown later in this paper, formation of an oxide having the maximum relative O concentration was necessary to cause restructuring of the metal surface leading to the activity enhancement.

Influence of Preoxidation on the Reactivity of Rh Single Crystals. Figure 1 shows the reactivity for *n*-pentane hydrogenolysis after the Rh single crystals were preoxidized at 70 Torr and 775 K. After oxidation of the crystal in the reaction chamber, the oxygen was evacuated and the crystal translated to the UHV chamber for measuring the surface composition by AES. The crystal was then translated back to the reaction chamber and the reaction carried out without any further treatment. After reaction, the surface of the crystal showed no O within the detection limits of AES (see Figure 4). This confirms that the reaction is being carried out over a metallic Rh surface. Indeed, when the oxidized Rh(100) crystal was exposed to 50 Torr of H_2 , the oxygen was reacted away by approximately 350 K. This is not surprising since rhodium oxide can be readily reduced by H₂ in supported Rh catalysts.¹⁶ Furthermore, the activity of the oxidized Rh surface after reduction in H_2 at 473 K was identical, within experimental error, with that where the reaction was carried out directly on the oxidized surface.

The activities shown in Figure 1 have not been corrected for any surface area increase in the metal due to oxidation-reduction. The activation energy for *n*-pentane hydrogenolysis was 22 kcal/mol over the preoxidized Rh surfaces. On both crystals there was an increase in activity due to the preoxidation. The increase in activity at a given temperature for the (100) surface was approximately 1 order of magnitude, but the actual increase for the



Figure 7. Reactivity of Rh single crystals for *n*-pentane hydrogenolysis as a function of pretreatment: (a, top) Rh(111); (b, bottom) Rh(100).

(111) surface depended on the reaction temperature due to the activation energy change after preoxidation. The increase in activity could be reversed by the cleaning procedure used for the Rh crystals. Figure 7 shows that the activity increase due to preoxidation was reversible on both the crystal orientations studied here.

The activity increase was dependent on the extent of oxidation as determined by AES. The correlation between *n*-pentane hydrogenolysis reactivity and surface oxygen concentration is shown in Figure 8. The activity increases gradually with increasing O concentration but a significant increase is not seen until the O concentration reaches its maximum value, which corresponds to a stoichiometry near Rh_2O_3 .

The hydrogenolysis selectivity on the preoxidized surfaces after oxidation of the Rh crystal at 70 Torr and 775 K for 1 h is shown in Figure 9. The selectivity did not depend on the orientation of the crystal and was markedly different from that on the annealed Rh surfaces shown in Figure 3. At low temperatures, the amounts of ethane and propane were equal and slightly greater than those seen on the annealed Rh(100) surface. The amount of methane, however, always exceeded that of *n*-butane by a significant amount, indicating that multiple hydrogenolysis must be occurring even at these low temperatures. At higher temperatures, the extent of multiple hydrogenolysis increased and led to a further increase in % methane at the expense of the higher hydrocarbons.

Hydrogenolysis Reactivity over Supported Rh/Silica. Figure 10 shows the TOF for *n*-pentane hydrogenolysis over 2% Rh/silica in the oxidized and annealed states. The oxidized state was obtained by heating the catalyst at 773 K in 70 Torr of O_2 overnight while the annealed state was obtained by heating the catalyst in 400 Torr of H_2 at 773 K overnight. The activation energy of the catalyst in the annealed state was 47 kcal/mol while, in the oxidized state, the activation energy dropped to 20 kcal/mol. The catalyst could be reversibly cycled between the oxidized and

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Figure 8. Effect of surface oxygen concentration after preoxidation on the reaction rate for *n*-pentane hydrogenolysis (a, top) Rh(111); (b, bottom) Rh(100).



Figure 9. Hydrocarbon product distribution over the preoxidized Rh single crystals: (a, top) Rh(111); (b, bottom) Rh(100).

annealed states in a manner similar to that shown for the single crystals in Figure 7. The hydrogenolysis selectivity was markedly



Figure 10. Specific reaction rate for *n*-pentane hydrogenolysis on annealed and preoxidized 2 wt % Rh/SiO₂ compared with that on Rh(111) as a function of temperature. The chemisorption uptake was not corrected for any increase caused by preoxidation. Previous work³ showed an increase in chemisorption uptake of no more than 30% due to the oxidative restructuring caused by preoxidation.



Figure 11. Hydrocarbon product distribution over 2 wt % Rh/SiO_2 during *n*-pentane hydrogenolysis (a, top) annealed in 600 Torr of H₂ at 773 K and (b, bottom) preoxidized in 70 Torr of O₂ at 773 K.

different in the two states as seen in Figure 11. Ethane and propane constituted approximately 70 mol % of the hydrocarbon products in the annealed state while their proportion dropped to ≈ 20 mol % in the oxidized state. The product distribution was very sensitive to even the slightest exposure of the catalyst to oxidizing conditions and the selectivity changed toward lower % ethane + propane. The activity and selectivity of the air-exposed catalyst lay somewhere between these two states and depended on the exact pretreatment history.

Transmission Electron Microscopy of Rh/SiO₂. The 2 wt % Rh/SiO₂ catalyst was examined by using 400-keV electrons in a JEOL JEM-4000 EX transmission electron microscope. The oxidation of Rh metal particles in this catalyst and the sample preparation have been described elsewhere.^{5,16} Figure 12a shows a micrograph of a Rh metal particle in this catalyst after annealing

Restructuring of Rhodium Metal Surfaces



Figure 12. Micrograph of Rh particle in the 2 wt % Rh/SiO₂ catalyst (a, top) after annealing in H₂ at 773 K and (b, bottom) after preoxidation in air at 773 K and treatment in H₂ at 323 K so as to partially reduce the oxide back to the metal.

in H₂ at 773 K at 600 of H₂. The Rh metal surface exhibits well-defined (111) and (100) facets as expected for fcc metals. It can be seen that the major facet is the (111) surface of Rh. After oxidation of this catalyst at 773 K in air, the catalyst was exposed to 200 Torr of H₂ at 323 K leading to partial reduction of the rhodium oxide to the metal. The particle imaged in Figure 12b, though substantially reduced into the metallic state, exhibits a highly twinned, nonequilibrium, internal structure. Observations of metal particles that have been similarly oxidized and reduced in H₂ at low temperatures (<573 K) confirm the absence of the relatively perfect facets such as those seen in Figure 12a in these metal particles.¹⁶ One might consider these surfaces as having been "roughened" due to the volume expansion upon oxidation and the inability of the metal to restructure into single crystals during mild reduction. While the micrographs in Figure 12 were not obtained from the same metal particle, we have previously reported the morphological transformations in a single metal particle exposed to oxidation-reduction cycles.³

Discussion

Influence of Surface Structure on n-Pentane Hydrogenolysis Reactivity. The selectivity for n-pentane hydrogenolysis is seen to be affected by crystal orientation and temperature (Figure 3). At low temperatures, scission of a single C–C bond occurs during the lifetime of the n-pentane on the surface and the amount of methane is equal to that of n-butane while the amount of ethane is equal to that of propane. Hydrogenolysis can therefore be construed to occur along parallel pathways, one involving scission of a terminal C–C bond (yielding methane and n-butane) and the other involving central bond scission (yielding ethane and propane). At low temperatures where single hydrogenolysis occurs, the Rh(111) surface produces nearly 70% ethane + propane. This implies that the probability of cleaving a primary-secondary (terminal) C-C bond is lower than that for cleaving a second-ary-secondary (internal) C-C bond. On the Rh(100) surface, cleavage of terminal C-C bond is favored by more than a factor of 2 over internal bond scission. The activation energies for the two pathways (terminal vs internal scission) are equal since the product distributions are invariant with temperature in the single hydrogenolysis regime.

At higher temperatures, methane becomes the major product on both Rh(111) and Rh(100) because the hydrocarbon fragments undergo successive demethylation. The onset of multiple hydrogenolysis coincides with the kink in the Arrhenius plot (Figure 1) and has been termed the "rollover" temperature¹⁹ in previous work. Under these conditions, the rate-determining step changes from C-C bond scission to product desorption. Reducing the hydrogen pressure during reaction has the same effect as increasing the temperature since both of these result in lowered surface coverage of hydrogen and lead to multiple hydrogenolysis of the adsorbed hydrocarbon. Hence the kink in the Arrhenius plot is not due to any irreversible changes (such as carbon accumulation) on the surface. Indeed, reactions performed in succession showed no temperature history in either selectivity or activity. A previous study has shown that the "rollover" temperature for n-butane hydrogenolysis occurred at a higher temperature on the Ir-(110)-(1×2) surface than the Ir(111) surface²⁰ consistent with the stronger binding of H₂ on the Ir(110)-(1×2) surface. Our results also show that rollover occurs at a slightly higher temperature on the Rh(100) surface compared to the Rh(111) surface.

The activation energy for *n*-pentane hydrogenolysis at low temperatures on Rh(111) is significantly greater (47 kcal/mol) than that on the Rh(100) surface (22 kcal/mol). The markedly different activation energies and different selectivities on these crystal surfaces suggest that the hydrogenolysis may proceed through a different intermediate on these two surfaces.

Effect of Preoxidation on the Reactivity of Rh. Oxidation of the Rh(100) and Rh(111) surfaces leads to an increase in activity and change in selectivity. The absence of any detectable surface oxygen after reaction implies that the reaction is occurring over a metallic Rh surface. The large excess of H_2 (20:1 H_2 :*n*-pentane) ensures very rapid reduction of the rhodium oxide to metallic rhodium at the reaction temperatures used. A separate prereduction step using H₂ at 473 K was used in some runs but did not affect the reactivity. It can be concluded that the reactivity changes are caused by morphological changes induced by oxidation-reduction cycles that persist during reaction conditions. The extent of self-annealing during reaction conditions is minimal, and it is possible to run subsequent reactions without any surface cleaning and obtain reaction rates that are identical with those obtained after directly oxidizing the metal surface. The surface cleaning procedure (involving heating the crystal to 1273 K) does anneal the surface and leads to a drop in hydrogenolysis activity (Figure 7). We attempted measurement of the metal surface area increase by using CO oxidation reactivities on the annealed and on the oxidized surface after the hydrogenolysis reaction. We found that the metal surface area increased by a factor between 2 and 3 as inferred from the CO oxidation rate enhancement. The measured increase in surface area was, however, dependent on the duration of the CO oxidation experiment, suggesting that the surface was being annealed by the CO oxidation reaction. Hence, since we were unable to quantify the surface area increase, we have not corrected the reactivities reported in Figure 1. The results show that the TOF for *n*-pentane hydrogenolysis increases after this oxidative-roughening of the metal surface. The increased activity is similar to that seen previously in ethane hydrogenolysis by Godbey et al.²¹ when a Pt(111) single crystal was roughened

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by Ar ion sputtering. However, since methane is the only product from ethane hydrogenolysis, it was not possible in the previous $study^{21}$ to infer precisely the nature of the changes in active sites.

The results from this study show that the active sites in the preoxidized rhodium metal surface are quite different from those on the annealed Rh(100) and Rh(111) surfaces. While the annealed metal surfaces exhibit single C-C bond cleavage from *n*-pentane at low temperatures, methane was the major product on the preoxidized surfaces even at the lowest temperatures examined by us, implying that multiple hydrogenolysis was occurring. Furthermore, the active sites on the preoxidized rhodium catalyst do not resemble those encountered as one reduces the rhodium metal particle diameter on Rh/SiO₂. Highly disperesed rhodium selectively cleaves the central bond in *n*-pentane yielding equal amounts of ethane and propane.¹⁴ The selectivity (% ethane + propane) for n-pentane hydrogenolysis on preoxidized Rh/SiO₂ is similar to that on the preoxidized Rh(111) as well as the Rh-(100) surface. This suggests that preoxidation yields a rhodium metal surface that is markedly different from that expected based on the orientation of the underlying metal substrate. The remarkable agreement between the supported catalyst and the single-crystal surfaces conclusively establishes that the silica support does not play a major role in the oxidative restructuring of the metal

Origins of the Surface Structure Changes Induced by Preoxidation of Rh. To understand better the changes in surface structure, we have studied the oxidation and reduction of small metal particles as well as single crystals of rhodium. We have observed^{5,7} that the oxide that grows epitaxially on Rh(111) at low temperatures (T < 773 K) has a lattice parameter that does not match that of Rh₂O₃. Furthermore, the average surface O concentration of this oxide by AES was approximately 0.5 implying a stoichiometry of RhO.⁷ Oxidation at higher temperatures (≈ 773 K) led to formation of Rh₂O₃.⁵ Therefore, it seems likely that the oxide that forms initially is cubic RhO which then transforms to polycrystalline Rh₂O₃^{5,10,16} and eventually to single-crystal Rh₂O₃ by 898 K.¹⁶ Differences in the reducibility of the rhodium oxides that have been seen by other workers^{22,23} may be related to these differences in the crystallinity of the oxide phase observed by TEM.^{5,16}

The transformation of rhodium to polycrystalline Rh_2O_3 during oxidation at 773 K leads to a 90% increase in volume. When the polycrystalline Rh_2O_3 is reduced at low temperatures such as those encountered during the hydrogenolysis reaction, the loss of oxygen and the shrinkage of the particle must occur under conditions where the mobility of metal atoms is fairly low. This leads to formation of polycrystalline Rh aggregates such as those seen in Figure 12b. These polycrystalline aggregates consist of small crystalline domains exposing significantly roughened surfaces.^{11,16} When the catalyst is reduced at temperatures >773 K, the greater mobility of the metal causes the surface to anneal and the selectivity of the annealed catalyst surface resembles that of the annealed Rh(111) surface. This is consistent with the TEM examination of the annealed catalyst that shows pronounced (111) facets of Rh (see Figure 12a).

The results obtained on the single crystals are in agreement with those on supported Rh. The initial oxide formed on the single-crystal surfaces, at relative O concentrations less than 0.5, causes only a small change the *n*-pentane activity (Figure 8). However, further oxidation of the Rh single crystals, leading to relative O concentration greater than 0.5, produces a more dramatic change in the *n*-pentane reactivity. The reactivity increase after the more severe oxidation can be explained by the presence of a roughened metal surface after reduction of Rh_2O_3 under reaction conditions. In summary, the surface structure changes due to oxidation-reduction are caused by the limited mobility of the Rh metal during reduction of the oxide at low temperatures. The differences in specific volume between Rh_2O_3 and Rh metal necessitate considerable restructuring of the surface leaving behind a roughened surface which anneals only after high-temperature treatment. These oxidation-induced reactivity changes are seen on both supported Rh and single crystals of Rh and therefore must be caused by intrinsic differences in surface structure and do not represent a support-induced effect.

Conclusions

n-Pentane hydrogenolysis has been studied on Rh(100) and Rh(111) single crystals and a supported Rh/SiO₂ catalyst to determine the effect of oxidation on Rh surface reactivity. The Rh(100) and the Rh(111) surfaces exhibited activation energies of 22 and 47 kcal/mol, respectively. At low temperatures, scission of only one C-C bond in *n*-pentane was observed at low conversions. The Rh(111) surface showed a preference toward scission of the central bond in the *n*-pentane molecule while the Rh(100) surface favored scission of the terminal carbon-carbon bond. These results suggest that the reaction on these two surfaces proceeds via different surface intermediates. The behavior of a 2 wt % Rh/SiO₂ catalyst after annealing in H₂ was similar to that of Rh(111) in activity, activation energy, and selectivity.

Oxidation of the Rh(111) and Rh(100) single crystals produced surfaces with almost identical activities and selectivities and appears to erase the differences between the (111) and (100) surfaces. The activation energy on the preoxidized surfaces was 22 kcal/mol, suggesting that the surfaces are much closer to the Rh(100)surface in the kinds of surface sites exposed. However, unlike on Rh(100), the hydrogenolysis of *n*-pentane on the preoxidized surfaces occurred with multiple cleavage of C-C bonds leading to methane as the primary product. The metal surface in the preoxidized catalyst is therefore quite different from any of the annealed single-crystal surfaces examined in this study. The behavior of the Rh/SiO₂ catalyst after preoxidation also mirrored the behavior of Rh(111) single crystal. Examination by TEM shows that Rh particles on this Rh/SiO₂ catalyst predominantly expose the (111) facets in the annealed state, but, after preoxidation and reduction at mild temperatures, the metal particles are polycrystalline aggregates with roughened surfaces. The remarkable agreement between the behavior of the single crystals and the 5-10-nm small particles provides clear evidence that the effects of oxidation and reduction are caused by intrinsic differences in surface structure and do not represent a support effect. The results demonstrate that the oxidation-reduction conditions used during the regeneration of Rh catalysts can influence the activity and selectivity quite significantly.

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