terium chemisorption. The catalysts were prereduced in D_2 for 3–4 h at room temperature in a standard gas titration apparatus. They were then evacuated under vacuum (10^{-4} mbar) overnight at 270 °C to yield the zero-valent clean metal surface. Deuterium was chosen over hydrogen to avoid the β-hydride phase formation and the deuterium titrations were performed with the catalyst heated to 100 °C as a further measure to avoid deuterium absorption in to the Pd bulk.[24]

Electron Microscopy Studies. The powdered $Pd/CaCO_3$ catalysts were crushed by an agate mortar and dispersed into suspension by shaking in ethanol. A drop of suspension was placed on a holey-carbon grid and allowed to dry. These specimens were examined in a JEOL JEM-200CX high resolution as well as in an analytical transmission electron microscope.

Auger Electron Spectroscopy. The Auger electron spectroscopic studies were obtained from the Charles Evans & Associates Materials Characterization Laboratories in Redwood City.

General Hydrogenation Procedure. Hydrogenations were carried out at ambient conditions in a three-necked round-bottom flask connected to a hydrogen reservoir maintained at normal pressure. The catalysts were placed in the flask and flushed several times with hydrogen to reduce surface oxides and remove any air from the apparatus. The catalysts were equilibrated in hydrogen for 30 min before solvent and reactant were added. For all the differently treated $Pd/CaCO_3$ catalysts, 24 ± 3 mg of catalyst, 10 mL of heptane, and 240 ± 60 mg of 2-hexyne were used. The selectivities of the Pd/C catalysts were determined with 40 ± 2 mg of catalyst and 38 ± 1 mg of 2-hexyne in 10 mL of *n*-heptane. All reactions on supported catalysts were stirred while the reactions on the foils were carried out unstirred. The foil reactions were carried out with 70 ± 15 mg of foil and 40 ± 10 mg of 2-hexyne in 5 mL of heptane, except in the case of the extensively used Pd foil that was treated with lead acetate where 417 mg of catalyst was used.

Acknowledgment. This work was supported by the Director, Office of Basic Energy Research, Office of Basic Energy Sciences, Materials Science Division of the U.S. Department of Energy under Contract No. DE-C03-76SF00098. J.G.U. is grateful for an Alberta Heritage fellowship. We acknowledge the help of Mr. Chuck Ecker with the analytical electron microscopy.

Registry No. $MeC{\equiv}C(CH_2)_2Me$, 764-35-2; Pd, 7440-05-3; $Pb(OAc)_2$, 301-04-2.

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[24] Benson, J. E.; Hwang, S.; Boudart, M. *J. Catal.* **1973**, *30*, 146.

Rational Design of a Heterogeneous Pd Catalyst for the Selective Hydrogenation of Alkynes

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Epitaxial palladium on tungsten film, which has a preferred (100) orientation, represents a rationally designed catalyst with a surface tailored to achieve high cis-semihydrogenation selectivity. Comparison with the Lindlar catalyst reveals improved cis selectivity and a much higher semihydrogenation selectivity. TEM studies provide evidence for bulk morphological changes of Pd foil that affect the selectivity of the hydrogenation reaction. Reactions on (111) and (110) Pd single crystals reveal a strong dependence of cis-selective semihydrogenation on the orientation of the metal, indicating surface structure sensitivity. Cyclic voltammetry is used to measure Pd foil surface areas and Pd foil was electrochemically roughened to alter its catalytic selectivity.

Introduction

Cis-selective semihydrogenation of alkynes on heterogeneous catalysts is the most important method for the generation of *cis*-olefins. The most widely used catalyst metal in this reaction, palladium, is employed in a variety of forms, which range from colloidal Pd and Pd black to Pd on various supports such as amorphous carbon, graphite, $CaCO_3$, $BaCO_3$, and $BaSO_4$. Much effort has been devoted to empirical modifications of such Pd-based catalysts to improve the desired selectivity.[1,2] One of the earlier modifications, the Lindlar catalyst (a $Pd/CaCO_3$ catalyst modified by reflux in a $Pb(OAc)_2$ solution)[3] applied in the presence of quinoline,[4] has remained the most popular catalyst for synthetic applications although high cis selectivity is also obtained with other modified catalysts.[2] Due to the lack of understanding and control, the success of such heterogeneous hydrogenation reactions in organic synthesis is still unpredictable and thus often considered unreliable. Alternative methods with homogeneous systems have been developed. Cis hydrogenation has been achieved with Li in THF,[5] Na/BF_3 in diglyme,[6] diisobutylaluminum hydride and methyllithium,[7] chloroborane,[8] palladium chloride in DMF,[9] zinc–copper couple,[10] $Rh(NBD)(PPhMe_2)_3$,[11] and CuI.[12] However, none of these

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[1] Rylander, P. *Catalytic Hydrogenation in Organic Syntheses*; Academic Press: New York, 1979. Freifelder, M. *Practical Catalytic Hydrogenation*; Wiley Interscience: New York, 1971. Augustine, R. L. *Catalytic Hydrogenation*; Marcel Dekker, Inc.: New York, 1965.

[2] Marvell, E. N.; Li, T. *Synthesis* **1973**, 457.

[3] Lindlar, H. *Helv. Chim. Acta* **1953**, *35*, 446.

[4] Isler, O.; Huber, W.; Ronco, A.; Kofler, M. *Helv. Chim. Acta* **1947**, *30*, 1911.

[5] Levin, G.; Jagur-Grodzinski, J.; Szwarc, M. *J. Org. Chem.* **1970**, *35*, 1702.

[6] Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1959**, *81*, 1512.

[7] Zweifel, G.; Steele, R. B. *J. Am. Chem. Soc.* **1967**, *89*, 5085.

[8] Brown, H. C.; Ravindran, N. *J. Org. Chem.* **1973**, *38*, 1617. Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1972**, *94*, 4370.

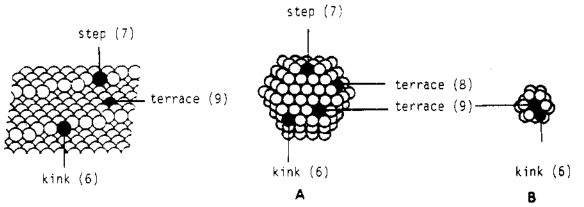
[9] Sisak, A.; Ungvary, F. *Chem. Ber.* **1976**, *106*, 531.

[10] Sondengam, B. L.; Charles, G.; Akam, T. M. *Tetrahedron Lett.* **1980**, *21*, 1069.

[11] Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 2143.

0022-3263/87/1952-3132$01.50/0

Scheme I. Comparison of Surface Atoms on a Bulk Metal and Cubo-octahedral fcc Metal Particles (Number of Nearest Neighbor Atoms Is Indicated in Brackets)

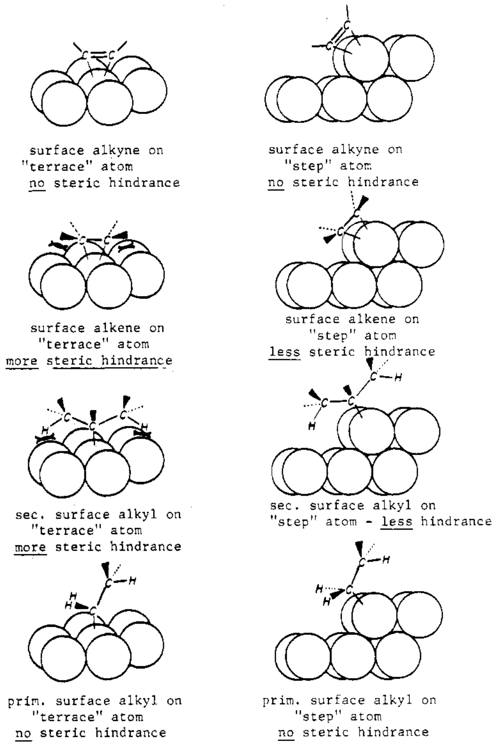


or other homogeneous methods have replaced heterogeneous Pd catalysts for cis-selective semihydrogenation which is still used in numerous total syntheses of natural products, including carbohydrates,[13] leukotrienes,[14] and prostaglandins.[15]

Considering the detailed mechanistic understanding of organic synthesis in general, it is surprising to note the almost complete lack of understanding of the factors that control selectivity and activity in the Pd-catalyzed hydrogenation of alkynes. From a molecular understanding of surface reactions introduced by surface science during the last decade,[16] the basic surface structure favoring the cis-selective semihydrogenation of alkynes should be determinable, thus providing a background for the rational design of a selective hydrogenation catalyst.

Although the hydrogenation selectivity is known to be sensitive to additives and catalyst preparation conditions,[17] the origin of side reactions in hydrogenation reactions is not known.[18,19] In a recent study of the semihydrogenation of phenylacetylene, it was reported that treatment of the Lindlar catalyst with a variety of transition-metal compounds resulted in an improvement of the semihydrogenation selectivity.[20] The use of equal weight of quinoline with Pd/BaSO$_4$ was found superior to the Pb(OAc)$_2$ treatment of the Lindlar catalyst.[21] One action of quinoline is to compete with freshly formed *cis*-alkene for surface sites, inhibiting alkene readsorption and subsequent reactions;[22] the other action is to facilitate morphological changes of the Pd particles.[23,24] The formation of large (metallic) Pd particles was proposed as the active and selective form of cis-selective semihydrogenation catalysts.[23] Examination of the effect of the lead acetate treatment on the selectivity of the Lindlar catalyst showed that the lead deposition is not necessarily related to the selectivity increase achieved. The selectivity increase is attributed to an increase of terrace Pd sites by lead deposition on stepped and kinked sites and by morphological changes brought about by the pretreatment procedure.[25]

Scheme II. Model of Steric Interactions of Hypothetical Surface Intermediates Bound to Terrace and Step Atoms



How can morphological changes affect the selectivity of hydrogenation reactions? This question can be answered by analyzing the major features of morphological changes on the atomic level. Morphological changes of metal particles are changes in particle size and shape. The surface structure of a fcc metal particle is essentially composed of three different types of surface atoms that are characterized by the number of nearest neighbor atoms. There are terrace atoms with nine (of (111) orientation) and eight (of (100) orientation) nearest neighbors, step (edge) atoms with seven, and kink (corner) atoms with six (or less) nearest neighbors. As shown in Scheme I, these atoms are present on bulk metal surfaces as well as on particles dispersed on supports. Their relative distribution changes with particle size, kinks being most prominent on small particles, terraces on large or bulk metal particles, and step atoms having a maximum at an intermediate particle size.[26] On bulk metals, such as single crystals and foils, the distribution of types of surface atoms is dependent on the orientation of the exposed crystal face, assuming the surface structure is a reflection of the bulk. The difference in free coordination sites suggests that these different surface atoms should exhibit different reactivities. Because of the additional complication of surface structure changes by reconstruction processes in the top layer (see below), accurate assessment of the relative concentration of surface atoms under liquid-phase reaction conditions is not possible. We therefore rely on a more simple differentiation where we term a surface rich in surface imperfections like steps and kinks a high energy surface and a smooth surface rich in terrace atoms a low energy surface. Morphological changes are, therefore, changes in the relative surface concentrations of these fundamental surface

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(12) Crandall, J. K.; Collonges, F. *J. Org. Chem.* **1976**, *41*, 4089.

(13) Jones, J. K. N.; Szaned, W. A. In *The Total Synthesis of Natural Products*; ApSimon, J., Ed.; Wiley Interscience: New York, 1981; Vol. 4, p 9–31.

(14) Rosenberger, M.; Newkom, C.; Aig, E. R. *J. Am. Chem. Soc.* **1983**, *105*, 3656. Cohen, N.; Banner, B. L.; Lopresti, R. J.; Wong, F.; Rosenberger, M.; Lui, Y.-Y.; Thom, E.; Liebman, A. A. *Ibid.* **1983**, *105*, 3661.

(15) Stork, G.; Raucher, S. *J. Am. Chem. Soc.* **1976**, *98*, 1583. Stork, G.; Kowalski, C.; Garcia, G. *Ibid.* **1975**, *97*, 3258. Corey, E. J.; Fleet, G. W. J.; Kato, M. *Tetrahedron Lett.* **1973**, 3963.

(16) Somorjai, G. A. *Chemistry in Two Dimensions*; Cornell University Press: Ithaca, NY, 1981.

(17) Petro, J. In *Contact Catalysis*; Szabo Z. G., Kallo, D., Eds.; Elsevier: Amsterdam, 1976 Vol II.

(18) Bond, G. C.; Wells, P. B. *Adv. Catal.* **1964**, *15*, 91. Clarke, J. K. A.; Rooney, J. J.; *Adv. Catal.* **1976**, *25*, 125. Gault, F. G. *Gazz. Chim. Ital.* **1979**, *109*, 255. Siegel, S. *Adv. Catal.* **1966**, *16*, 124.

(19) Burwell, R. L., Jr. *Chem. Rev.* **1957**, *57*, 895.

(20) Rajaram, J.; Narula, A. P. S.; Chawla, H. P. S.; Dev, S. *Tetrahedron* **1983**, *39*, 2315.

(21) Cram, D. J.; Allinger, N. L. *J. Am. Chem. Soc.* **1956**, *78*, 2518.

(22) Dobson, N. A.; Eglinton, G.; Krishnamurti, M.; Raphael, R. A.; Willis, R. G. *Tetrahedron* **1961**, *16*, 16.

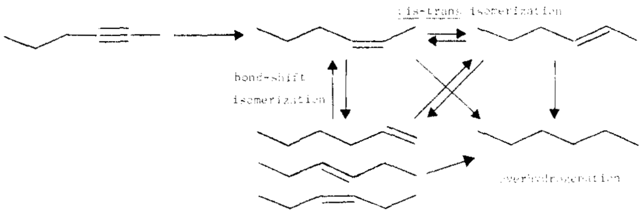
(23) McEwen, A. B.; Guttieri, M. J.; Maier, W. F.; Laine, R. M.; Shvo, Y. *J. Org. Chem.* **1983**, *48*, 4437.

(24) Maier, W. F.; Chettle, S. B.; Rai, R. S.; Thomas, G. *J. Am. Chem. Soc.* **1986**, *108*, 2608.

(25) Ulan, J. G.; Maier, W. F. *J. Org. Chem.*, in press.

(26) Van Hardeveld, R.; Hartog, F. *Adv. Catal.* **1972**, *22*, 75.

Scheme III. Reaction Network of 2-Hexyne Hydrogenation



sites. It follows that, in order for morphological changes to affect the selectivity found in alkyne hydrogenation reactions, these reactions must be sensitive to the surface structure of the catalyst particles. This appears to contrast Kung et al.'s conclusion on the structure insensitivity of the 3-hexyne hydrogenation on supported Pt over a range of catalyst dispersions.[27] However, the data obtained on Pt did not include very low dispersions found with bulk metals and results on Pt do not necessarily apply to Pd. An experimental examination of our hypothesis was therefore still warranted.

Of the various aspects of hydrogenation reactions that might be sensitive to metal surface structure, the most obvious and simple are steric effects. Some hypothetical steric interactions likely to be encountered during alkyne hydrogenation reactions are indicated in Scheme II. For steric reasons, initial formation of π-adsorbed alkenes as well as secondary surface alkyls should be more hindered on terraces than on surface imperfections (steps or kinks) while surface alkynes or primary surface alkyls should encounter little difference in the steric interactions on these sites (see Scheme II). In addition, rotation about the C–C bond, necessary for cis–trans isomerization, might be more easily accomplished on a stepped surface. Any loss in cis selectivity could then be correlated with the concentration of steps and kinks. If alkyne and alkene indeed differ in their sensitivity to active-site geometry, then manipulation of the catalyst's surface should be the key to the control of selectivity. However, it should be emphasized that the representations in Scheme II are only models. These surface intermediates have been postulated before to explain hydrogenation reactions[18] and seem reasonable choices although none of which have yet been identified on a Pd surface during hydrogenation reactions.

Results and Discussion

2-Hexyne was chosen as a model compound for this hydrogenation study because it is an asymmetric internal alkyne whose initial semihydrogenation product, *cis*-hexyne, is prone to cis–trans and bond-shift isomerization and overhydrogenation. The reaction network displayed in Scheme III indicates the major products observed. *cis*-2-Hexene, the desired product, was well separated on our GC column. The presence of *trans*-2-hexene, 1- and 3-hexenes, and *n*-hexane indicates the degree to which side reactions are occurring. *n*-Hexane and 1-hexene are well-separated, while the isomeric 3-hexenes have a similar retention time on our SE-30 column as the *trans*-2-hexene. This lack of detail does not affect the selectivity number, which is the % *cis*-2-hexene. It is important to point out that selectivity numbers referenced in this paper do not refer to selectivities at low conversion but to the total product maximum of *cis*-olefin, which corresponds to yield. It has become common practice in the literature to cite maximum "selectivities" at lower conversion. This is misleading, since we find that selectivities of 96–98% can be achieved readily at conversions below 50% (see reaction profiles below). The true selectivity of a catalyst for alkyne hydrogenation, however, is only revealed at higher or complete conversion. Although zero-order behavior in alkyne was obtained under all reaction conditions upon stirring or shaking, reactions were conducted without any agitation. This had the advantage of reducing the reaction rate at the time when the reaction approached the maximum of *cis*-olefin concentration, which ensured accuracy of this important number obscured very easily at zero-order conditions.

We used only bulk metal catalysts in this study to avoid the problems associated with the separation of support effects (mass transport phenomena, metal support interaction, Brønsted sites), uncontrollable morphological changes, and particle size effects on the rate and selectivity of this reaction. On a bulk metal the geometrical surface area is constant while on supported catalysts there is the possibility that small particles migrate and fuse. The use of bulk metal catalysts therefore ensures that turnover frequencies, N_f (reacted molecules per surface atom and second), is meaningful. A drop in N_f can be assumed to reflect surface deactivations by poisoning or carbonation effects and not changes in total surface area while a increase in N_f must reflect surface roughening. In all cases catalytic activity of our catalyst was restored completely upon catalyst oxidation excluding uncontrollable poisoning effects. N_f values given throughout this work are based on geometrical surface areas and are not corrected for surface roughness.

Palladium, in contrast to Pt or Rh, has the important property of forming a β-hydride phase in the presence of hydrogen, a process that is slow but unavoidable at normal hydrogen pressure.[28] This β-hydride phase, which contains about 0.6 H atom per Pd, has the same orientation as the bulk Pd,[29] but its lattice parameters differ due to a lattice expansion of about 6%. β-Hydride, known to be catalytically active, has been made responsible for morphological changes of Pd particles at reaction conditions.[30]

Cis hydrogenation of alkynes is commonly conducted in the presence of modifiers (usually quinoline) known to compete successfully with olefins for surface interactions[24] and thus increase the selectivity while reducing the overall reaction rate.[31] To ensure that the data were not obscured by such effects, this study was conducted in the absence of any modifiers.

1. Single Crystal Study. The surface structure sensitivity of alkyne hydrogenation was tested by the hydrogenation of 2-hexyne on properly cut Pd single crystals of (111) and (110) orientation (see Figure 1).

The maximum cis selectivity obtained with the (111) single crystal was 87%. In contrast, the (110) single crystal was found to be extremely unselective. The maximum concentration of *cis*-2-hexene was only 37% of the total reaction mixture and by the time alkyne was completely consumed the concentration of the isomerized alkenes had far surpassed *cis*-2-hexene. The strongly increased tendency for overreduction on this single-crystal surface indicates that the dominance of stepped surface atoms on a (110) plane correlates with the active sites for isomeri-

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[27] Kung, H. H.; Pellet, R. J.; Burwell, R. L., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 5603.

[28] Wicke, E., Brodowsky, H. In "Hydrogen in Metals", *Topics in Applied Physics*; Völkl, J., Alefeld, G., Springer Verlag: Berlin, 1978; Vol. 28.

[29] Palczewska, W. *Adv. Catal.* **1975**, *24*, 245. Paal, Z.; Menon, P. G. *Catal. Rev.-Sci. Eng.* **1983**, *25*, 229.

[30] Maier, W. F. *Proc. 10th Org. React. Catal. Soc.*, in press.

[31] Steenhoek, A.; van Wijngaarden, B. H.; Pabon, H. J. J. *Recl. Trav. Chim. Pays-Bas* **1971**, *90*, 961. Bond, G. C.; Wells, P. B. *Adv. Catal.* **1964**, *15*, 155.

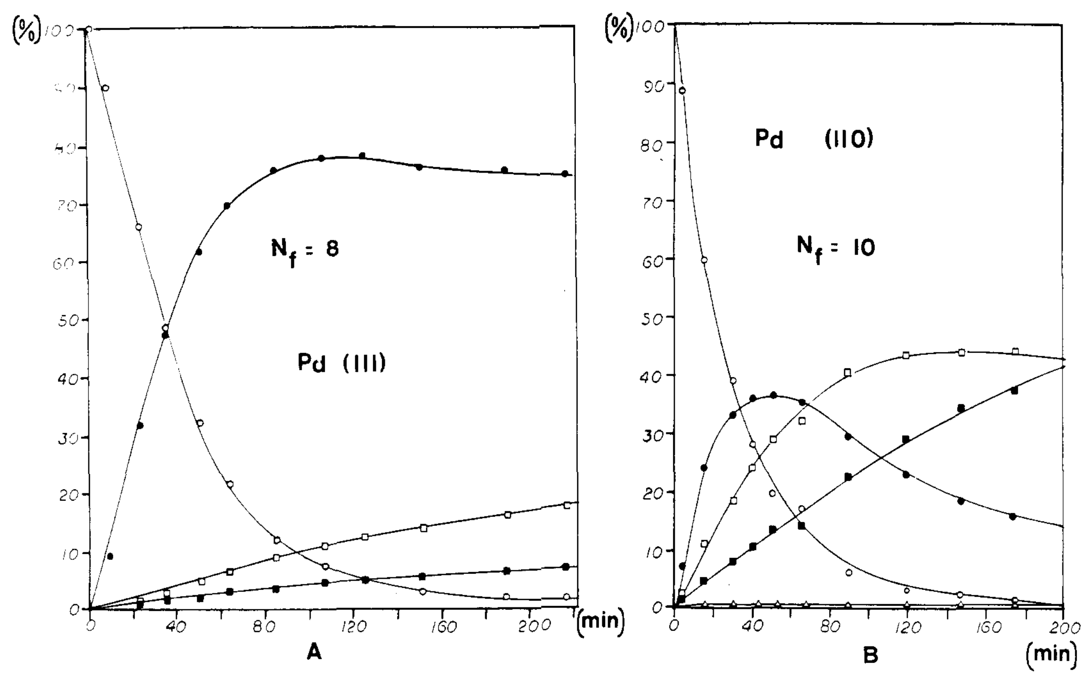

Figure 1. Reaction profile of 2-hexyne hydrogenation on (111) and (110) Pd single crystal: ○ = 2-hexyne; ● = *cis*-2-hexene; □ = *trans*-2-hexene and 3-hexenes; ■ = *n*-hexane; △ = 1-hexene.

zation and olefin hydrogenation. Such a conclusion is not surprising in light of a number of similar recent observations. On the basis of a Pd particle size analysis, stepped surface atoms were also proposed to correlate with the isomerization of (+)-apopinene on Pd and Pt.[32] Rorris et al. report a maximum in the turnover frequency for propylene hydrogenation on supported Pt and Pd catalysts at 60% dispersion,[33] which seems to correlate with a maximum in the % edge character (stepped surface atoms) exposed. Siegel and Hawkins obtained evidence for a surface structure sensitivity of alkyne hydrogenation by the selective poisoning of the cis-hydrogenation sites for di-*tert*-butylacetylene.[34]

It seems disappointing to find that the "ideal" surface of the (111) single crystal does not give 100% selectivity. However, in a more detailed study on the mechanism of the cis-selective semihydrogenation of alkynes, gas-phase experiments at low conversion point to an intrinsic unselectivity of this reaction independent of the surface structure, suggesting that both 5% of the side products (mainly *trans*-alkene and alkane) are formed directly from the alkyne on the catalyst surface.[35] In addition, the single-crystal edges comprise 15% of the total surface. The structure of these edge areas is unknown and may account for part of the side reactions obtained. Furthermore, after one reaction in which the (111) crystal had been exposed to hydrogen and hydrocarbon for over 20 h, the surface was covered with three sets of fine parallel cracks oriented in 60% angles of each other reflecting the (111) surface orientation. Such visible fracturing, which may be explained by the lattice expansion upon formation of the β-hydride phase of Pd, most likely causes roughening of the single-crystal surface, which may contribute to the nonideal selectivity. This hypothesis is supported by the loss of the Pd single crystal's mirror perfect polished appearance during the experiment, pointing to macroscopic surface roughening.

How meaningful are results obtained with properly cut single crystals under liquid-phase conditions? It should be pointed out that in the above experiments we rely on the assumption that the bulk structure and orientation of the Pd also resembles the surface structure. No evidence for massive changes of the orientation of surface layers relative to bulk structures under liquid-phase hydrogenation conditions has been obtained. TEM studies on the structure of supported metal particles have revealed that the surface layer of such particles is no different than those observed in surface studies.[36] The most common conditions in which surface reconstructions have been observed were on ultraclean surfaces of single crystals with higher energy surface structures like (100) and (110).[37] The reconstructions obtained under such artificial conditions are limited to the top surface layer and can be interpreted as an attempt of the surface atoms to make up for the lack of surface coordination by increasing the number of nearest neighbors atoms through hexagonal or other close packing. (110) surfaces of Pd are known to reconstruct in a (2 × 1) overlayer in the absence[38] and in the presence of hydrogen,[39] which does not change the dominance of surface imperfections (step or kink sites) relative to the dominance of terrace atoms on a (111) surface. (111) Pd surfaces are not known to reconstruct; on the contrary, evidence for the increase of the (111) texture upon multiple exposure of Pd surfaces to β-hydride formation has been presented.[38] Conservation of the bulk orientation of our (110) single crystal after hydrogenation reactions was confirmed by the Laue pattern of the used crystal. It seems therefore safe

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[32] Smith, G. V.; Ostgard, D.; Bartok, M.; Notheisz, F. *Proc. 10th Org. React. Catal. Soc.*, in press. Notheisz, F.; Bartok, M.; Ostgard, D.; Smith, G. V. *J. Catal.* **1986**, *101*, 212.

[33] Rorris, E.; Butt, J. B.; Burwell, R. L., Jr.; Cohen, J. B. *Proc. 8th Int. Cong. Catal. Berlin* **1984**, IV 321.

[34] Siegel, S.; Hawkins, J. A. *J. Org. Chem.* **1986**, *51*, 1638.

[35] Ulan, J. G.; Maier, W. F. *Langmuir*, submitted.

[36] Yacaman, M. J.; Gomez, A. *Appl. Surf. Sci.* **1984**, *19*, 348. Yacaman, M. J.; Chabes-Retchkiman, P. *Surf. Sci.* **1984**, *144*, 1439. Yacaman, M. J. *Chem. Phys. Solid Surf.* **1984**, *5*, 183.

[37] Cattania, M. G.; Penka, V.; Behm, R. J.; Christmann, K.; Ertl, G. *Surf. Sci.* **1983**, *126*, 382. Van Hove, M. A.; Koestner, R. J.; Stair, P. C.; Biberian, J. P.; Kesmodel, L. L.; Bartos, I.; Somorjai, G. A. *Ibid.* **1981**, *103*, 218.

[38] Barnes, C. J.; Ding, M. Q.; Lindroos, M.; Diehl, R. D.; King, D. A. *Surf. Sci.* **1985**, *162*, 59.

[39] Cattania, M. G.; Penka, V.; Behm, R. J.; Christmann, K.; Ertl, G. *Surf. Sci.* **1983**, *126*, 382.

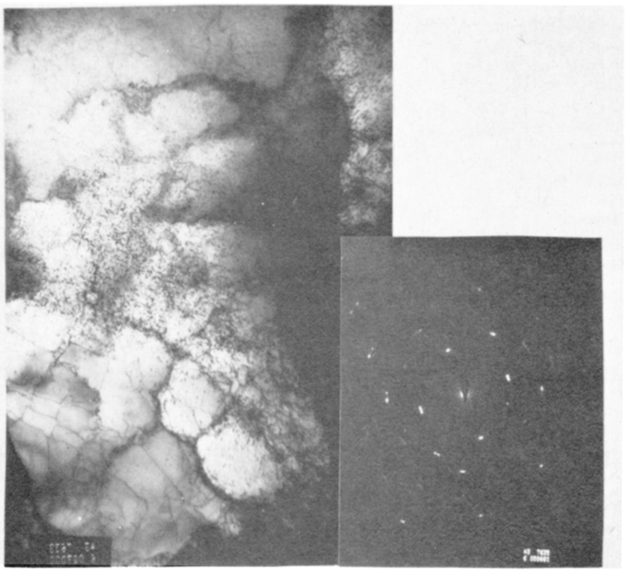

Figure 2. TEM micrograph of a grain of the fresh Pd foil with associated diffraction pattern (magnification 23 000).

to conclude that under our mild liquid-phase conditions the surface composition of the crystals reflected the bulk orientation and the low selectivity observed on the (110) oriented crystal correlates with the much higher concentration of surface imperfections relative to the (111) surface. The high turnover frequencies obtained on both crystals are strong evidence against the interference of trace impurities, especially in the case of the less selective (110) crystals, whose slightly increased reaction rate relative to the (111) crystal correlates with the increased surface roughness rather than with the presence of surface impurities which would act to block active sites.

Although these experiments have shown that there is indeed a strong correlation between surface structure and selectivity in alkyne hydrogenation reactions, problems in a direct transformation of these findings into the preparation of catalysts with oriented surfaces can be expected from the apparent instability of the palladium structure.

2. Pd Foil Study. Since single crystals are not practical catalysts for hydrogenation reactions, further studies were performed on Pd foil, which has been found highly selective for alkyne hydrogenations.[23] Any fcc metal foil is composed of individual grains which, to a rough approximation, can be represented by equiaxed particles of cubo-octahedral shape. Auger electron spectrum of a freshly oxidized Pd foil showed mainly Pd, some surface oxygen, and little carbon (uncorrected intensity of AE signals at 270 eV(C, Pd):330 eV(Pd):510 eV(O) 1:2:1) while the spectrum of the used Pd foil mainly differed in the intensity of the carbon peak (peak ratio 2.5:1:0.6). Traces of sulfur and chlorine were detectable on the used foil. The TEM of the unused Pd foil showed a large grain size of about 20 μm (200 000 A). The grains show braids of dislocation and subboundaries characteristic of a worked metal. The major orientation was found to be (100). Figure 2 shows a representative micrograph (brightfield picture) together with the associated electron diffraction pattern documenting the (100) texture found as the preferred orientation of most of the grains. The broadening of the dots indicates small rotations as expected by the nature of the worked material. A typical product composition achieved with this Pd foil is 90% *cis*-2-hexene, 7% isomerized disubstituted hexenes, and 3% *n*-hexane at complete conversion of the 2-hexyne. The reaction profile for Pd foil is shown in Figure 3.

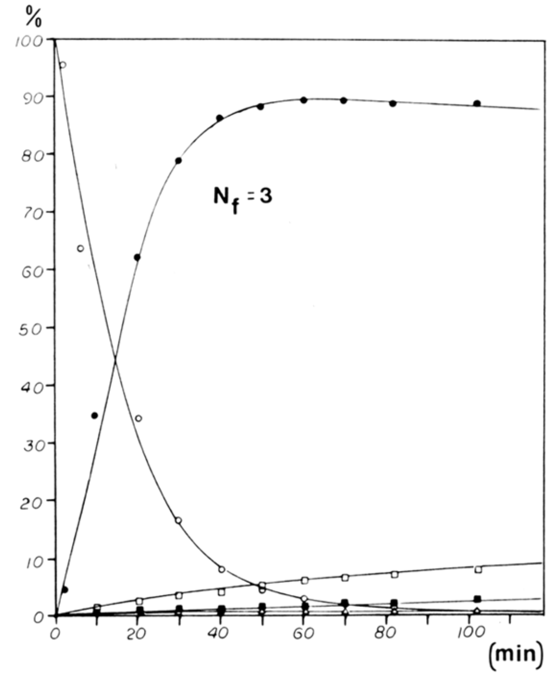

Figure 3. Reaction profile of 2-hexyne hydrogenation obtained on new Pd foil. Symbols are identical with those used in Figure 1.

Table I. Effect of Pretreatment on N_f and Selectivity of the Hydrogenation of 2-Hexyne on Pd Foil

pretreatment	N_f	cis selectivity, %
oxygen, 600 °C, 2 h	3	91
exposure to reaction conditions for 350 h	2	72
nitrogen, 1000 °C, 12 h	3	89
hydrogen, 800 °C, 18 h same foil, N_2 annealed after extensive use	3	72

It has been suggested by Janko et al. that randomly oriented polycrystalline Pd films undergo a low temperature rearrangement with repeated hydrogen treatment, which results in the formation of a (111) texture.[40] Because Pd foil is so easy to reclaim and reuse, it was of interest to test whether this conclusion also holds for the bulk Pd foil under normal reaction conditions. Table I summarizes the effect of various Pd foil treatments on selectivity and activity of 2-hexyne hydrogenation. Three sequential reactions were run on Pd foil (36 cm^2 geometrical surface area) in which 40, 90, and 700 mg of 2-hexyne were hydrogenated, corresponding to a turnover number of 10^5 molecules/surface atom. During these experiments (total reaction time 60 h) the turnover frequency was found to drop gradually from 3 to 2, which is attributed to carbonation effects. The foil remained exposed to reaction conditions (in the last reaction solution) for an additional 100 h, after which it was found to have lost all its activity. Oxidation of the foil at 500–700 °C in O_2 for several h restored activity and selectivity. In general it was found that Pd foil that had been exposed to reaction conditions for a fairly brief time of about 3 h, then oxidized in O_2 at 400–600 °C, and reduced in H_2 at room temperature reproducibly maintained a selectivity of 90%.

However, Pd foil that had been exposed to reaction conditions for much longer (400 h) lost all activity and, after oxidation in O_2 at 500 °C for 2 h and reduction in hydrogen at room temperature for 15 min prior to reaction,

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[40] Janko, A.; Palczewska, W.; Szymerska, I. *J. Catal.* **1980**, *61*, 267.

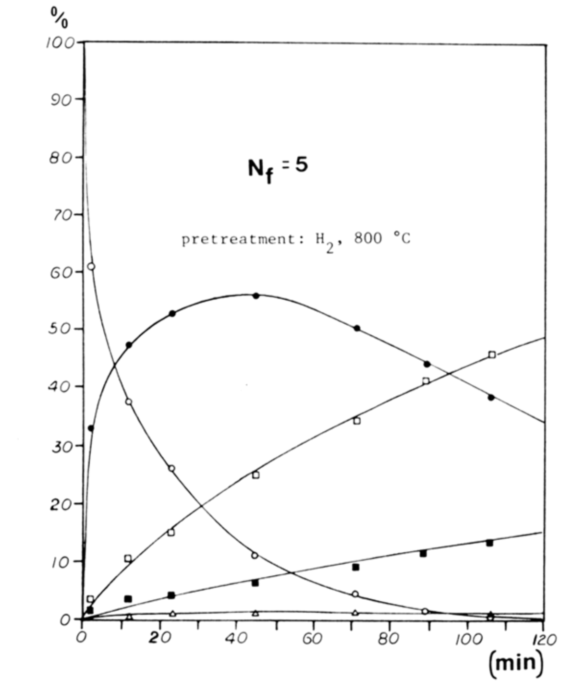

Figure 4. Reaction profile of 2-hexyne hydrogenation on Pd foil after hydrogen annealing of the Pd foil at 800 °C. Symbols are identical with those used in Figure 1.

completely regained its activity but remained significantly less selective. Even prolonged and repeated oxidation and reduction treatments could not restore the original selectivity of the Pd foil. Annealing this unselective foil in N_2 for 24 h at 1000 °C reestablished activity and selectivity (90%). Since such an annealing process can be expected to result in the formation of a smoother surface (more low energy terraces), the observed increase in selectivity supports the correlation of low-energy terrace-type surfaces with selectivity. The recovery of the original selectivity by this annealing process also indicates that the loss of initial selectivity may be linked to a steady increase of higher energy sites. The reaction profiles obtained after oxidation and N_2 annealing are superimposible with that of the unused foil (see Figure 3).

In contrast, annealing the foil in H_2 at 800 °C for 12 h resulted in a drop in selectivity to 56%, indicating a buildup of sites responsible for the undesired side reactions by the high temperature action of the hydrogen. Poisoning processes due to impurities are unlikely since the unselective foil had the same activity as the new selective foil and exposure to the same hydrogen at room temperature did not result in such a significant loss of selectivity. The change in selectivity was therefore attributed to a major morphological change of the Pd structure, most likely due to the high diffusivity of Pd for hydrogen at such high temperatures. Some of the selectivity (82%) could be restored by prolonged heating in N_2 at 1000 °C, but the original selectivity of 90% was never regained. The profile obtained after H_2 treatment (see Figure 4) shows the low selectivity and an increased rate of *cis*-2-hexene consumption. The rather high turnover frequency, evidence against any poisoning effects, points to an increase of the number of exposed surface atoms, which implies an increase of the surface roughness supporting the above hypothesis.

Prolonged use of this foil resulted in further loss of selectivity, which leveld out to 72%. All attempts to increase this selectivity by high temperature nitrogen annealing failed and no further drop in selectivity was observed. The foil, by this time, had been exposed to a high temperature hydrogen treatment and to reaction conditions for over 2000 h, corresponding to a turnover number of about 5 × 10^6 molecules of alkyne per surface atom. Since significant poisoning effects are ruled out by the high activity and by AES data, structural changes of the surface reflecting changes in the bulk structure of the Pd foil have to be postulated for this loss in selectivity of the bulk Pd metal. Transmission electron microscopy studies of the used Pd foil confirmed this hypothesis.

Figure 5. TEM micrograph of unselective Pd foil (bright field picture obtained from (200) ring).

The TEM study of this used Pd foil showed a drastic change in material structure. The average grain size is reduced (500–10 000 Å) and the clean curved grain boundaries are indicative of recrystallization. The representative micrograph in Figure 5 shows mixed orientations of the grains. The formation of voids not present in the fresh foil was also detected. Twinned structures were quite common in the unselective material, while no twins could be detected in the unused foil sample. The diffraction pattern (not shown) confirmed the randomness of the orientation. The data support the above hypothesis that structural changes in Pd foil correlate with the change in catalytic selectivity in agreement with above single-crystal experiments. It should be emphasized that such a drastic change in the bulk structure of a solid noble metal is rather unusual, especially considering the rather mild conditions applied. The reaciton profile of the 2-hexyne hydrogenation on this unselective foil (Figure 6) shows the increased rate of the alkene consumption noted before.

The fact that the oxidation treatment always recovers the initial activity but not the original selectivity indicates that carbonation is more likely linked to deactivation, but not to the selectivity properties of the catalyst. The conclusion is supported by the Auger electron spectroscopy data reported above, which show a significant increase of the amount of surface carbon on the Pd foil after use. Whether there is a contribution of this surface carbonation to the loss in selectivity cannot be determined from our data, since the loss in activity is always much faster than the loss in selectivity.

3. Electrochemical Study. A supplementing electrochemical study was conducted to further confirm that the selectivity of the hydrogenation of 2-hexyne is surface structure sensitive. The total surface area of the foil used

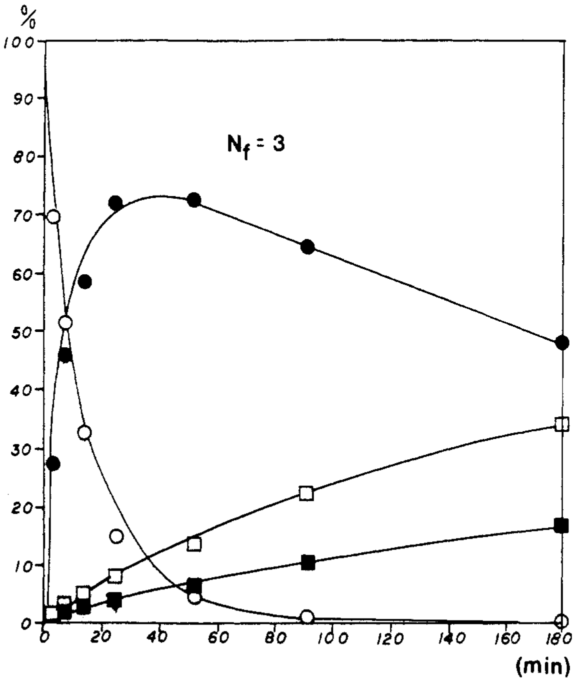

Figure 6. Reaction profile of 2-hexyne hydrogenation obtained on the used Pd foil with of low selectivity (corresponding to Figure 5). Symbols are identical with those used in Figure 1.

in these experiments was determined by cyclic voltammetry. The method used utilizes the hysteresis of the oxygen adsorption process, which allows the determination of the real surface area on Pd electrodes.[41] When this technique was applied to the fresh Pd foil, a roughness factor of 1.1 (actual surface area is 1.1 × the geometrical surface area) was obtained (see Figure 7a).

The reaction profile of the foil after surface area determination shows no change in selectivity (identical with that shown in Figure 1), which indicates that this electrochemical measurement, while known to roughen the surface somewhat, does not affect the surface structure of the Pd foil enough to alter the catalytic behavior. Pd foil was roughened mechanically with abrasive to test the sensitivity of this electrochemical method and, as shown in Figure 7, determination of the active metal surface area showed a significant increase to a roughness factor of 1.7. The reaction profile with this mechanically roughened Pd foil exhibited only marginal loss of selectivity. Mechanical roughening exposes large regions of the Pd surface, but it would probably not increase the relative concentration of steps and kinks by very much, so a higher activity was seen due to the increase in total number of exposed sites. In order to roughen the metal surface more effectively, the foil was electrochemically oxidized. Pd, in contrast to Pt or Rh, does not exhibit limiting oxide coverage, since it experiences submonolayer oxide formation (see the sharp rise in current at potentials at about 1.7 V in Figure 7). After oxidizing the Pd foil at 2.0 V (SCE) for 4 min, the surface area determination shown in Figure 7b gave a roughness factor of 8, indicating that sublayer oxidation had been achieved. This bulk surface oxidation could also be recognized by the dull brown appearance of the foil surface. When this foil was exposed to hydrogen, instant color change to black indicated effective reduction and a very rough surface. The reaction profile of this electrochemically modified foil in Figure 8 shows the expected large drop in catalytic selectivity (almost as unselective as the (110) single crystal), which is again attributed to a change in surface structure, this time brought about by surface oxidation. Participation of Pd(II) is unlikely since it is unstable in an ambient hydrogen atmosphere. Comparison of the low selectivity Pd catalysts (see Figures 1b, 4, 6, and 8) shows that the drop in selectivity is always connected to an increase in the rate of *cis*-2-hexene consumption. The turnover frequencies of the alkyne hydrogenation remain constant and are apparently rather structure insensitive.

Table II. Comparison of Selectivity and N_f of the Hydrogenation of 2-Hexyne on Metal Foil Catalysts at Room Temperature and 1 Atm Hydrogen in *n*-Heptane

catalyst	N_f	cis selectivity, %
Pd foil	4	90
Pt foil	5×10^{-2}	65
Rh foil	0.1	53
Rh foil after annealing in N_2	1×10^{-2}	40
Ni foil	2	86
$Pd/Rh_{0.23}$ foil	5	87

4. Hydrogenation Activity of Some Bulk Metals. The use of bulk metal foils as catalysts also provides an opportunity to compare the hydrogenation activity of Pd, Pt, Rh, and Ni (see Table II) in their bulk form. All foils were oxidized at 700 °C and reduced prior to the reaction with 2-hexyne. The Rh and the Pt foil were found to be much less active and selective than the Pd and the Ni foil. Annealing of both the Rh and the Pt foil at 1000 °C in nitrogen before reaction resulted in a further decrease of the N_f to <0.01. On Rh and Pt, overhydrogenation dominates the reaction. This order of magnitude difference in the bulk hydrogenation activity between Ni, Pd and Rh, Pt can be attributed to the ability of Pd and Ni to adsorb hydrogen into its bulk lattice, a property not shared by Rh and Pt.

Catalyst Design

The above experiments consistently support the conclusion that terrace surfaces represent the most selective surface structure for cis-selective semihydrogenation. The selectivity appears to originate from a decrease in the rate of *cis*-olefin reactions (isomerization and hydrogenation) with decreasing surface imperfections and not from the alkyne hydrogenation itself, whose rate is unaffected by different surface orientations.

We have also found that Pd, even in its bulk metallic form, is subject to surface and bulk rearrangement processes in the presence of hydrogen. Because of this apparent instability of the Pd surface and its bulk structure under reaction conditions, stabilization of the structure of the Pd is a requirement for a selective hydrogenation catalyst. One possible way to achieve such stabilization of the bulk structure is through the formation of alloys. Rh, a metal with similar catalytic properties as Pd but much stronger lattice energies as reflected in a heat of atomization of 134 kcal/mol (compare to 90 kcal/mol for Pd), should thus induce morphological stability (Pd–Rh alloys). A Pd/Rh (30% Rh) foil was studied for stabilizing effects. The freshly oxidized Pd/Rh foil had a N_f of 5 and a selectivity of 87%. However, it lost activity much more rapidly than Pd foil. In analogy to pure Pd foil the activity could be restored with high temperature oxidation. However, the selectivity of this alloy was not stable to long exposure to reaction conditions either. After 4 weeks of immersion in heptane, there was a considerable drop in selectivity reminiscent of the Pd foil. As the Pd/Rh foil did not present an improvement over Pd foil, work in this area was not continued.

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[41] Rand, D. A.; Woods, R. *J. Electroanal. Chem.* **1971**, *31*, 29.

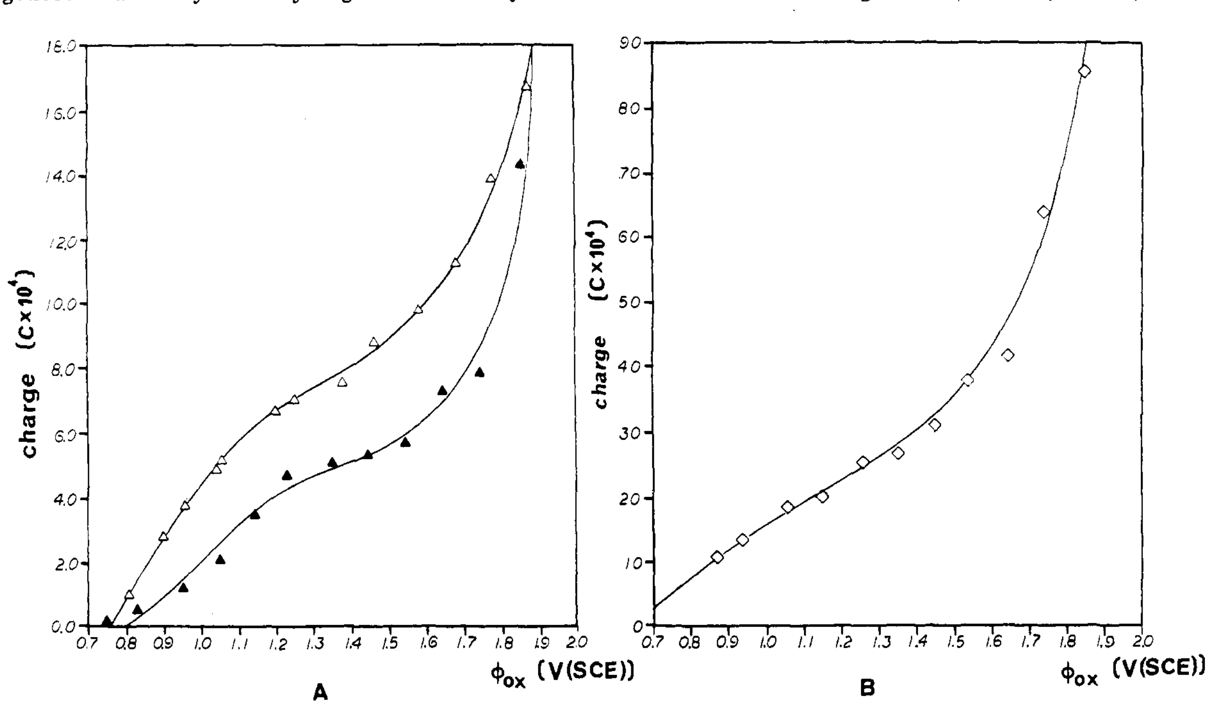

Figure 7. Dependence of the oxygen reduction peak area on the anodiazation potential for surface area determinations of new Pd foil (▲), scratched Pd foil (△), and Pd foil after electrochemical oxidation for surface roughening (□).

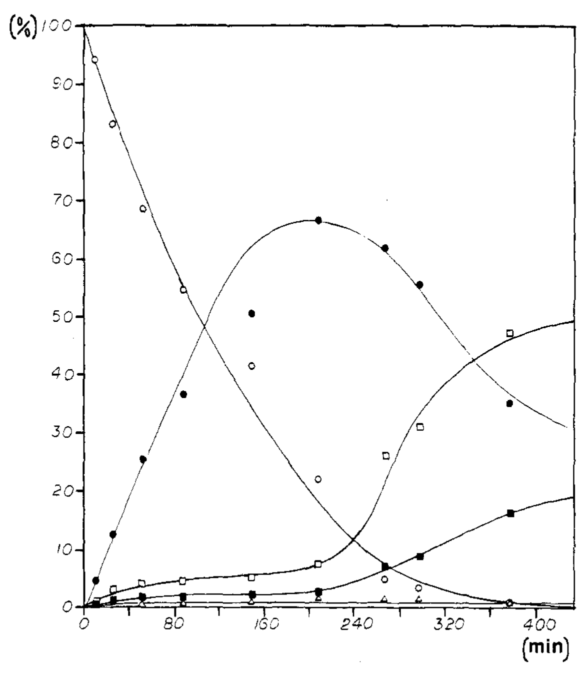

Figure 8. Reaction profile of Pd foil after electrochemical roughening (surface oxidation) with 2 V/vs. SCE for 4 min. Symbols are identical with those used in Figure 1.

Another way to stabilize bulk structures is by use of a suitable support. In the case of Pd, use of epitaxial Pd films appeared to be an attractive possibility. Pd films of (111) orientation can be grown on mica and have shown to become continuous at a thickness of about 300 Å.[42] It was also shown that the (111) Pd planes are oriented parallel to the surface on mica as well as on MgO. However, it was found that the growth of Pd on MgO is two-dimensional (pseudomorphic layer by layer growth with periodic misfit dislocations due to the lattice mismatch) whereas on mica three-dimensional growth is observed that is attributed to the change in metal support interaction.[43] By TEM it was shown that Pd on MgO, formed by vapor-phase deposition, does grow in perfectly epitaxial layers even at room temperature.[44] A surface study of Cu and Pd films on mica revealed the formation of perfect (111) orientation at about 500-Å film thickness.[45] On NaCl surfaces Pt films grow in a polycrystalline fashion at lower temperatures, but at temperatures greater than 400 °C epitaxial growth is observed that provided (100) Pt orientations.[46] Such epitaxial (111) and (100) Pt films, grown on (111) and (100) NaCl have been used to study the activity for the catalytic hydrogenolysis of methylcyclopentane.[44]

In metal on metal systems with similar lattice parameters, a pseudomorphic layer by layer growth is observed.[47] However, good lattice fit and proper surface preparation appear to be most important for the display of bulk-like properties in the film after deposition of only monolayer concentrations.[48] An empirical treatment of the epitaxial growth mode of metals on metals based on geometrical considerations is given by Bauer.[49]

We examined Pd thin films on a variety of support materials like MgO, quartz, sapphire, mica, CaF_2, and W foil.[50] The most promising results were obtained with the Pd/W film. The rationale for the preparation of the Pd/W film was to provide a stable interface and the hope that the strong lattice energy of the metallic W will induce additional stabilization of the Pd surface film. Since no high temperature treatment is involved in the film preparation, alloying should only occur directly in the interface and not at the surface of the Pd film which could be confirmed by AES (lack of W on the Pd film surface). A

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(42) DeCooman, B. C.; Vankar, V. D.; Vook, R. W. *Surf. Sci.* **1983**, *128*, 128.

(43) Garmon, L. B.; Doering, D. L. *Thin Solid Films* **1983**, *102*, 141.

(44) Heinemann, K.; Osaka, T.; Poppa, H.; Avalos-Borja, M. *J. Catal.* **1983**, *83*, 61.

(45) Christmann, K.; Ertl, G. *Thin Solid Films* **1975**, *28*, 3.

(46) Gehrer, E.; Haydek, K. *Thin Solid Films* **1984**, *115*, 283.

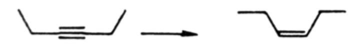
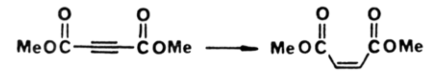
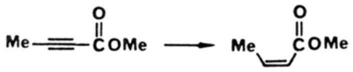
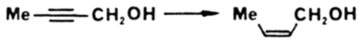
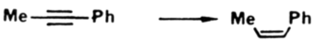
(47) Matthews, J. W. *Surf. Sci.* **1972**, *31*, 241. Yagi, K.; Takayanagi, K. Kobayashi, K.; Honjo, G. *J. Cryst. Growth* **1971**, *9*, 84.

(48) Jona, F.; Strozier, J. A., Jr. In *Epitaxial Growth*; Matthews, J. W., Ed.; Academic Press: New York, 1975.

(49) Bauer, E. *Appl. Surf. Sci.* **1982**, *11/12*, 479. Lawless, K. R. *Physics of Thin Films*; Hass, G., Thun, R. E., Eds.; Academic Press: New York, 1976; Vol. 4.

(50) Maier, W. F.; Smith, D. A., unpublished results.

Table III. Comparison of the Cis Selectivity (*S*) and Overhydrogenation Selectivity (*O*) between the Pd/W Film and a Commercial Lindlar Catalyst in the Hydrogenation of Various Alkynes[a]

	Pd/W film		Lindlar cat.		
	S	*O*	*S*	*O*	N_f
	88	(200)	86	(2.6)	2.0
	90	(22)	78	(1.1)	2.0
	87	(550)	74	(3.7)	1.1
	92		89	(177)	0.1
	94	(17)	90	(3.7)	0.1
	78	(1.5)	90	(0.2)	0.3
	86		89	(4)	0.02

[a] *S* = maximum concentration of *cis*-olefin in the reaction profile. *O* = ratio of N_f alkyne over N_f *cis*-olefin. N_f = turnover frequency of the alkyne observed on the Pd/W film.

technical problem encountered with all but the Pd/W film is the lability of the interface under reaction conditions. The Pd films were found to fracture and peel off upon the action of solvent and hydrogen, indicating facile penetration of the metal support interface by substrate and solvent in the presence of hydrogen. The only thin film that remains unchanged and stable is the Pd film on W foil, which was therefore also selected for further mechanistic studies.[35] The films (300 Å) were characterized by TEM before and after exposure to reaction conditions as well as to 12-h reflux in xylene under hydrogen in the presence of the modifier quinoline. The Pd/W films exhibit a strong (100) orientation (see representative microdiffraction pattern, and dark field TEM picture in Figure 9). The morphological stability of the Pd/W film under organic reaction conditions and exposure to modifiers was confirmed by the TEM pictures (see Figure 9b). While the electron diffraction patterns show no significant difference, the dark field TEM pictures, obtained from the (200) ring, indicate a clear increase in the proportion of (100) oriented particles after the exposure to reaction conditions. The bulk orientation of the Pd film on W actually improves with use rather than deteriorates. Initial tests with a 1000-Å Pd film on W confirmed that these films exhibit similar activity and selectivity as the annealed Pd foil for 2-hexyne hydrogenation. In unstirred reactions the overhydrogenation on the films is much slower than on the Pd foil and the films appear to be stable to reaction conditions, maintaining a selectivity of about 90% after over 150 h of exposure (slow deactivation is probably due to poisoning). Direct interference of the tungsten support can be excluded by the complete lack of hydrogenation activity for 2-hexyne with W foil. Such films therefore appear to be the most selective form of Pd and the 90% selectivity achieved supports the above suggestion about the intrinsic formation of side products. It seems that the 99% selectivity for alkyne hydrogenation reported by Schrock and Osborn with homogeneous rhodium complexes[11] cannot be obtained with heterogeneous Pd catalysts.

The hydrogenation selectivity of this Pd/W foil was compared with that of a commercial Lindlar catalyst on a variety of alkynes. The reactions were carried out in the absence of any modifiers. The results are summarized in Table III. In most of the cases the Pd/W shows a higher cis-semihydrogenation selectivity than the Lindlar catalyst. The relative rates of alkyne reactivity on the Pd film is included in the form of the turnover frequency N_f. The rate of alkene hydrogenation of the methylstyrene and the dimethyl maleate were too slow for a determination of the overhydrogenation activity. More important than the cis selectivity, however, is the much higher overhydrogenation selectivity of the Pd/W film relative to the Lindlar catalyst, which is demonstrated by the reaction profiles of the hydrogenation of 2-hexyne on the Pd/W foil, on the Lindlar catalyst, and, for comparison, on a commercial 10% Pd/C catalyst (see Figure 10).

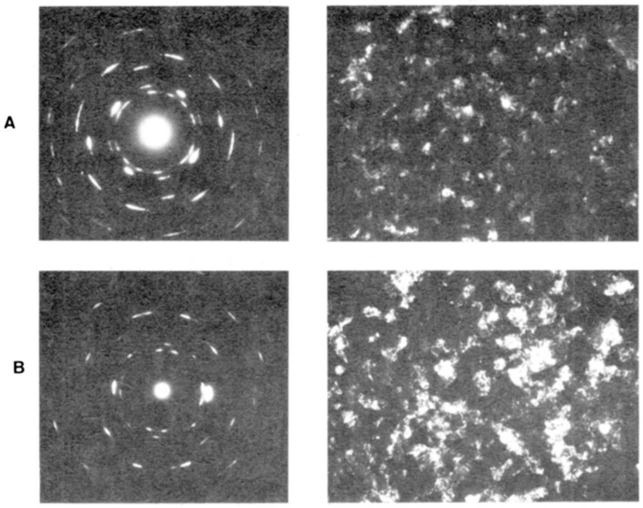


Figure 9. Microdiffraction pattern, dark field images, and reaction profile of Pd/W films. (A) TEM diffraction pattern and dark field image from (200) ring of fresh Pd/W film; (B) TEM diffraction pattern and dark field image from (200) ring of Pd/W film after reflux in xylene in the presence of quinoline and hydrogen for 12 h followed by the hydrogenation of 30 mg of 2-hexyne.

Conclusion. We have successfully prepared the first rationally designed heterogeneous catalyst with a surface tailored towards an improved hydrogenation selectivity demonstrating that the main features which control selectivity in heterogeneous hydrogenation reactions can be identified and converted into the preparation of catalysts with selectivity properties comparable to the best empirically developed catalysts. The Pd/W catalyst developed presents an improvement over the popular Lindlar catalyst with respect to overhydrogenation and selectivity, but it also has clear limitations. The Pd/W film can be highly

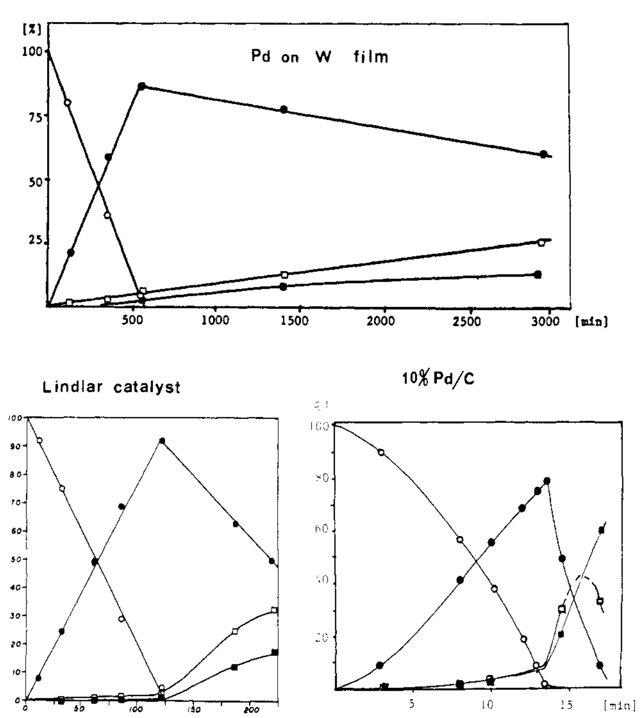


Figure 10. Reaction profiles of the 2-hexyne hydrogenation with Pd/W film, commercial Lindlar catalyst, and a commercial 10% Pd/C catalyst (stirred conditions).

recommended for the hydrogenation of small amounts (1–10 mmol) of alkynes. Due to the small active surface area, the conversion of larger amounts of substrates will require inconvenient reaction times and catalyst deactivation due to the presence of impurities may be encountered frequently. For the conversion of small amounts of substrates, however, it has the advantage of facile and quantitative product recovery, essentially no workup, slow overhydrogenation, and does not need additional modifiers like quinoline. In addition, the reaction rate is proportional to the geometric surface area of the film and thus readily controllable.

Our study provides strong indications that the hydrogenation of alkynes on solid Pd surfaces is structure sensitive, a characteristic important for the understanding of such catalytic processes. However, in light of the morphological instability of Pd particles in the presence of hydrogen, this structure sensitivity is of little value as long as we cannot ensure a stable surface structure of the Pd particles.

The lack of complete selectivity on the stable Pd/W surface indicates to us that the intrinsic formation of side products cannot be overcome as long as we work with exposed metal surfaces and the desired preparation of catalysts with ultimate hydrogenation selectivities can only be accomplished with entirely new approaches to heterogeneous catalysts. One such approach, where we separate the hydrogen activation by the transition metal from the actual catalyst surface by thin film deposition techniques is presently being pursued in our laboratories.

Experimental Section

Unless otherwise noted, hydrocarbons of purity greater than 99% were obtained commercially and used without further purification. The Lindlar catalyst was obtained from Aldrich. The hydrogenations were monitored with a HP5890A gas chromatograph equipped with a methyl-silicone capillary column (60 m SPB-1 from SUPELCO) and FID detector. Product composition and yields were obtained from integration of the GC peaks by a Hewlett Packard 3390A integrator and are uncorrected GC area %. The products of hydrogenation of all alkynes were identified by coinjection with authentic samples. In the case of 1-(methoxycarbonyl)-1-propyne, 1-phenyl-1-propyne, and 2-butyn-1-ol where the alkene standard consisted of a mixture of cis and trans isomers, the initial major reaction product was the cis isomer. In all cases the cis isomer was well separated from any other compound; only 3-hexyne required cooling of the GC column to 10 °C to separate *cis*-3-hexene from *trans*-2- and -3-hexenes.

The surface area of the foils, films, and single crystals was assumed to be the geometric surface area. The number of exposed sites was calculated from the surface area of the catalysts with the conversion factor 1.5×10^{15} surface atoms/cm^2 of metal surface. The selectivity is the percentage *cis*-2-hexene at complete consumption of alkyne. The overhydrogenation selectivity (O) is calculated as the rate of initial N_f of alkyne consumption over N_f of *cis*-olefin consumption during the same experiment. N_f is determined from the slope of substrate disappearance from 0% to 50% conversion. For the Lindlar catalyst the total surface area was not known so O was calculated from the number of molecules reacted/gram of Pd and seconds.

Pd (111) and (110) Single Crystals. General Pretreatments. The single crystals were cut to the proper orientation (±1 °C) and polished. Correct bulk orientation was confirmed by Laue X-ray back-scattering. Immediately before use the (110) single crystal was oxidized at 400 °C in O_2 for 2 h. After one use the (111) single crystal showed some warping. The crystal was cut in half and repolished by using standard metallurgical techniques. The Laue pattern indicated that, though it had been damaged, it still retained bulk crystal ordering. One-half of this newly polished single crystal was annealed at 400 °C in N_2 for 4 h before a reaction was repeated.

Pd Foil. General Pretreatment. Prior to use, Pd foil was heated in a Lindberg oven at 600 °C for 2 h in O_2 to remove carbon impurities. **Nitrogen Pretreatment.** The oxidized foil was heated to 1000 °C for 12 h in N_2. **Hydrogen Pretreatment.** The oxidized foil was heated to 800 °C for 18 h in H_2.

Pd/Rh Foil. General Pretreatment. Pd/Rh foil alloy (60% Pd) was heated in O_2 at 600 °C for 2 h and then reduced in H_2 for 1 h at 100 °C. **Heptane Pretreatment.** The foil was stored in 5 mL of heptane for 4 weeks before undergoing the general pretreatment.

Pt Foil. General Pretreatment. Pt foil was oxidized in O_2 at 700 °C for 4 h and then reduced to H_2 at 400 °C for 3 h. **Nitrogen Pretreatment.** The Pt foil was oxidized at 700 °C in O_2 for 4 h, reduced in H_2 at 400 °C for 2 h, and then heated in N_2 at 1000 °C for 15 h.

Rh Foil. General Pretreatment. Rh foil was oxidized at 700 °C in O_2 for 2 h and then reduced in H_2 at 400 °C for 2 h prior to reaction. **Nitrogen Pretreatment.** The Rh foil was oxidized at 700 °C for 2 h in O_2, reduced at 400 °C in H_2 for 2 h, and then heated in N_2 at 1000 °C for 20 h.

Ni Foil. Ni foil was used without pretreatment.

Pd/W Film. The Pd/W films were prepared by Krypton sputtering of Pd on W heated to 253 °C at a pressure of 1.7×10^{-7} Torr (sputter rate 23 Å/min). The W foils were cleaned by preheating for 30 min to 1000 °C. Films used had a Pd thickness varying from 400 to 900 Å. These films cannot be cleaned of carbon deposits by heating in oxygen as the tungsten is oxidized.

Electrochemistry. General Procedure. Electrochemical experiments were carried out at 25 °C in 1 M H_2SO_4 prepared from distilled and purified water. The solutions were deoxygenated with nitrogen prior to use. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the working electrode via a reference electrode bridge tube equipped with a Vycor frit also filled with 1 M H_2SO_4. All potentials refer to the SCE. Potentials were controlled with an EG&E Model 362 scanning potentiostat. Voltamograms were recorded on an Omega RD 200XY recorder and for the surface area calculations the potential vs. time curves were plotted on a strip-chart recorder. The working electrode consisted of a circular piece of Pd foil, encased in an EG&G Flat Specimen Holder (Model K105), used in the EG&G standard corrosion cell (Model K47). A 1 cm^2 area was exposed to the acid solution. The working electrode was pretreated by potential cycling between 0.2 and 1.2 V at 20 mV s^{-1} until the scans were reproducible.

The generation and determination of the oxygen coverage is achieved by stepping the potential quickly (500 mV s^{-1}) from 0.2

V to its new potential (O_{ox}) where it is held for 40 s (T_{ox}). The potential is then returned to 0.2 V at the rate of 20 mV s^{-1}, the hysteresis of the surface oxide being recorded at this time. The solution is quickly purged with nitrogen to return it to the initial conditions and the CV is obtained from 0.2 V to 1.2 V and the returning to 0.2 V at a rate of 20 mV s^{-1}. When the potential O_{ox} is greater than 1.2 V, the procedure is modified slightly. After the potential is held at O_{ox} for T_{ox}, it is quickly lowered (500 mV s^{-1}) to 1.2 V and held for 30 s, during which time the solution, especially in the region directly surrounding the working electrode, is purged vigorously with nitrogen. Dissolved oxygen in solution formed during T_{ox} interferes with the determination of surface oxide and must be removed in this manner. The potential is then returned to 0.2 V at 20 mV s^{-1} and later the CV is obtained between 0.2 and 1.2 V.

The amount of surface oxide formed at O_{ox} during T_{ox} is determined from the charge passed (Q_{ox}) in reducing the layer in the following potential sweep. Values of Q_{ox} were obtained by integrating the cathodic oxygen reduction peak on the voltammetric curve. The current following the peak was used as the base line for integration. The electrode surface was found to roughen slightly during the experiment especially for values of O_{ox} greater than 1.3 V. This change in surface roughness was corrected for by measuring the charge corresponding to the cathodic reduction of oxygen adsorbed during the CV from 0.2 V to 1.2 V Q_{std} (which became larger as the surface became rougher) and multiplying Q_{ox} by the ratio of Q_{std} (beginning of the experiment) to Q_{std} (after each O_{ox}). O_{ox} was varied from 0.7 V to 1.9 V. The charge Q_{ox} was plotted vs. O_{ox} and the value of Q at which the graph levels off was taken as the point where monolayer coverage is achieved. Assuming the surface is composed of equal parts (111) and (100) faces and formation of surface oxide involves a 2 e process with one oxygen atom formed on each surface Pd atom, then every 424 μC corresponds to 1 cm^2 of Pd atoms. The true surface area of the Pd foil can be obtained and the surface roughness calculated.

Electrochemical Pretreatment. Pd foil was placed in the flat specimen holder of an EG&G Electrochemical Corrosion cell filled with degassed 1 M H_2SO_4. The voltage was quickly set to 2 V (SCE) and held for 4 min. The Pd surface went through several color changes (yellow, orange, pink, blue) and oxygen was liberated from the oxidation of water. The circuit was broken and the foil removed, the other side exposed, and the process repeated. The roughened foil's surface area was then determined. Because of the instability of the roughened surface this measurement was found to substantially decrease the surface roughness. For the catalytic experiments, new, identically electrochemically pretreated foil was used, and it's surface roughness was assumed to be identical with that determined above. Immediately prior to the hydrogenation of 2-hexyne the foil was reduced in H_2 gas very thoroughly to ensure that Pd oxides were not present which may change the selectivity.

Hydrogenation Procedure. All hydrogenations were preformed at room temperature in a three-necked, round-bottomed flask connected to a hydrogen reservoir maintained at ambient pressure. The catalyst was placed in the flask and flushed with H_2 several times to reduce surface oxides and to remove any air. For the single crystals (surface area of 6 cm^2), 3 mL of heptane and to 0.25 mmol of 2-hexyne were used. For the Pd, Pt, Ni, Pd/Rh, and Rh foil experiments 20–30 cm^2 of catalyst foil surface, 0.5 mmol of alkyne, and 5 mL of solvent were used. For the Pd foils used in the electrochemical experiments a total surface of 2 cm^2 times the roughness factor, 0.25 mmol of 2-hexyne, and 5 mL of solvent were used. For the Pd/W films 6 cm^2 catalyst surface area, 0.5–2 mmol alkyne, and 5 mL of heptane were used except in the hydrogenation of dimethyl acetylenedicarboxylate where the solvent was THF. For the Lindlar reactions 20 mg of catalyst, 3 mmol of alkyne, and 10 mL of solvent were used.

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Registry No. Pd, 7440-05-3; W, 7440-33-7; 1-hexyne, 693-02-7; 2-hexyne, 764-35-2; 3-hexyne, 928-49-4; dimethyl butynedioate, 762-42-5; methyl 2-butynoate, 23326-27-4; 2-butyn-1-ol, 764-01-2; 1-propynylbenzene, 673-32-5.