the spectrum after the pressure had stabilized. The position of maximum absorbance of the π,π^* band was assigned by taking the median of the two frequencies on either side corresponding to 90% of the maximum absorbance. Each value given in the table is the average of three individual determinations at each density. The monochromator was calibrated with holmium oxide.

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Effect of Lead Acetate in the Preparation of the Lindlar Catalyst

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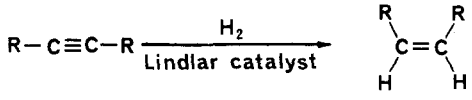
The effect of the Lindlar treatment in the preparation of Pd catalysts for the cis-selective hydrogenation of alkynes is investigated with hydrogenation studies on 2-hexyne. The study emphasizes the effect of lead on the hydrogenation selectivity of Pd catalysts. The role of the additives in the catalysts is examined by transmission electron microscopy. The effect of lead deposition on the catalytic activity and selectivity of Pd surfaces is studied with lead-coated Pd foils. No selectivity enhancing effects of the deposition of lead on the Pd particles could be identified.

Cis-selective semihydrogenation of alkynes is receiving on-going attention[1] as an important step in organic synthesis to introduce functionality and stereochemistry simultaneously. A variety of heterogeneous catalysts exist for this transformation, which vary in type of support, added modifiers, and reaction conditions but invariably contain palladium. Despite 35 years of research, the Lindlar[2-4] catalyst, used in uncounted natural product syntheses, still remains the most popular catalyst for this cis-selective semihydrogenation of alkynes.[5]



The Lindlar catalyst is a $Pd/CaCO_3$ catalyst treated with lead acetate solution and used in the presence of 0.05–1 molar equiv of quinoline. One well-established action of the quinoline is to inhibit alkene surface interactions, which results in an overall selectivity increase,[6a] a general concept in selective hydrogenation reactions.[6b] An undesired side effect is that quinoline also competes with alkynes for Pd surface interaction, which reduces the overall reaction rate.[7] Quinoline's action as a promoter of morphological changes of the Pd particles, which seems to contribute to the selectivity increase, has been recognized only recently.[7] A study on the effect of catalyst support on alkyne hydrogenation showed $BaSO_4$ to be superior to $CaCO_3$, the only advantage of the latter was a more effective inhibition of the polymerization side reaction with 1,4-butynediol.[8] Very little is known about the action of the lead acetate treatment. Our interest in this popular catalyst was stimulated by the expectation of finding and characterizing some form of lead deposition on the palladium particles responsible for the selectivity properties. Such a material could then be synthesized in a controlled fashion and might lead to better catalysts. Doubts about the superior properties of the lead acetate treatment have been raised by Allinger and Cram, who reported improved selectivity obtained with $Pd/BaSO_4$ in the presence of quinoline.[9] In studies on the partial hydrogenation of 1,4-butynediol Fukuda could only detect reduced catalyst activity with increasing amounts of lead acetate in the Lindlar treatment.[10] It needs to be determined if the lead in fact affects the selectivity of the Pd catalysts at all and if so, what is the exact nature of its effect.

Lindlar had already recognized in his original paper[3] that the treatment produces a deposit of metallic lead on the palladium. In a surface science study concerning the effect of lead deposits on Pd (111) single crystals, it was found that lead has little effect on the shape and maxima position of the temperature-programmed desorption spectra of hydrogen but did decrease the amount of chemisorbed hydrogen, indicating only inhibiting effects were operat-

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ing.[11] In fact, hydrogen chemisorption was completely inhibited with only 0.3 monolayers of lead on both sides of the single crystal. The only chemical evidence for the formation of a new surface compound was obtained with the thermal desorption of acetylene, which, although hard to detect, achieves a maximum at 0.2 monolayer coverage of lead, coinciding with the $(3^{1/2} \times 3^{1/2})$ overlayer. The only evidence that lead may affect the selectivity of the semihydrogenation of alkynes was indicated by a drastic decrease of ethylene chemisorption. At a surface concentration of only 0.03 monolayer of lead, adsorbed ethylene was barley detectable by TPD (temperature-programmed desorption) and disappeared completely at higher coverages.[11] The higher selectivity of Pd_3Pb alloy for acetylene[12] and 2-butyne[11] hydrogenations compared to the Lindlar catalyst led to the suggestion that a surface alloy of the composition Pd_3Pb is formed as the active species of the Lindlar catalyst.[13] However, no evidence for such a compound was detected on the Lindlar catalyst nor was comparative evidence supporting the superiority of the Pd–Pb alloy provided.[12] A distinct poisoning effect for the hydrogenation activity of Pd upon addition of Pb(II) was noted by Jenkins, while little poisoning was observed with metallic lead deposition.[14]

Speculation on the importance of trace impurities has resulted in the development of an improved Lindlar catalyst by subsequent treatment with a $MnCl_2$ solution.[15] However, the study was limited to a terminal alkyne (phenylacetylene), so stereospecific semihydrogenation was not addressed.

Since selectivities of reactions are a direct function of the extent of side reactions, knowledge about their origin is important. In a recent study on the origin of side reactions in hydrogenation reactions it was shown that cis–trans isomerization, bond shift isomerization, and overhydrogenation, the major side reactions in the cis-selective hydrogenation of alkynes, are surface structure sensitive and occur most readily on rough surfaces rich in surface steps or kinks.[16] Terrace surfaces were found to be the most selective sites for alkyne hydrogenation because of the high structure sensitivity of alkene hydrogenation and isomerization reactions while alkyne hydrogenation itself is structure insensitive. It was found that disubstituted alkenes are not hydrogenated at all on epitaxial Pd/W film believed to represent stable terrace surfaces while terminal olefins were found to hydrogenate readily on all Pd surfaces.[16] Other evidence for such structure sensitivity of olefin hydrogenation reactions was reported recently by Smith et al., who attribute the isomerization of (+)-apopinene to the extent of edge (step) surface atoms;[17] by Rorris et al., who report a maximum in the turnover frequency for propylene hydrogenation on supported Pt and Pd catalysts at 60% dispersion,[18] which again may correlate with a maximum in the % edge character (stepped surface atoms) exposed; and by Siegel and Hawkins, who obtained evidence for surface structure sensitivity by the selective poisoning of the cis hydrogenation sites.[19] On the basis of such results the effect of the lead acetate treatment in the Lindlar procedure on the morphology and structure of the Pd catalyst has to be considered as a possible origin of the observed selectivity enhancement not necessarily related to the chemical nature of the lead itself.

Table I. Selectivities and Rates of 2-Hexyne Hydrogenation at Standard Conditions with the Catalysts Indicated

catalyst	CHS,[a] %	N_f	cis/trans ratio	SHS[b]
$Pd/CaCO_3$	77	4.0	6.4	85
$Pd/CaCO_3$, aged for 4 months	88	4.0	15	97
$Pd/CaCO_3$ Lindlar conditioned	91	0.5	38	99
commercial Lindlar catalyst	78		3.4	87
Pd foil	90	3.0	15	96
Pd foil plated with lead <monolayer	80	0.2	7.1	94
Pd foil plated with lead >monolayer	68	0.3	4.1	88
Pd foil with lead film (300 Å)	67	0.8	5.1	86
new Pd foil, Lindlar conditioned	82	0.1	7.3	95
unselective Pd foil, Lindlar conditioned	88	0.02	19	99
Pd foil Lindlar conditioned and oxidized	50	1.2	2.6	78
10% Pd/C	79	1.5	8.8	89
10% Pd/C after 4 h H_2 treatment at 400 °C	90	3.4	16	97

[a] Cis hydrogenation selectivity = maximum of *cis*-2-hexene formation on the reaction profile. [b] Semihydrogenation selectivity = % olefins in the product at the maximum of *cis*-2-hexene.

Results and Discussion

In the following study based on the hydrogenation of 2-hexyne, we examined the effect of the lead acetate treatment on the morphology of the $Pd/CaCO_3$ catalyst as well as on the selectivity of alkyne hydrogenation. Only reproducible selectivities are reported. While the reactions on the supported catalysts were stirred to avoid mass transport problems, the reactions on the foils (no mass transport problems) were conducted without stirring. Although zero-order behavior in alkyne was obtained readily with the foil catalysts upon stirring or shaking, these reactions were conducted without agitation. This had the advantage of reducing the reaction rate at the time when the reaction approached the maximum *cis*-olefin concentration. Control experiments showed that under our conditions there was no difference in the maximum selectivity with or without stirring. In fact, the selectivities obtained without stirring are usually slightly higher because it is less likely to miss the actual selectivity maximum. Stirring was found to mainly increase the rate of side reactions aggravating the exact determination of the selectivity maximum. Although the ratio of exposed Pd surface to substrate in the experiments with supported catalysts was higher than in the foil experiments, control experiments over a wide range of concentrations showed that the selectivity obtained under our conditions was not affected by this ratio. The selectivity of differently treated Pd foils was compared to obtain a reliable measure of the effect of lead deposits on the catalytic reaction. Pd foil was chosen to eliminate any particle size effect and support interactions and to obtain a direct measure of the effect of lead deposition on catalytic properties. Quinoline was omitted from the reaction conditions to ensure that changes in catalyst characteristics were due solely to the

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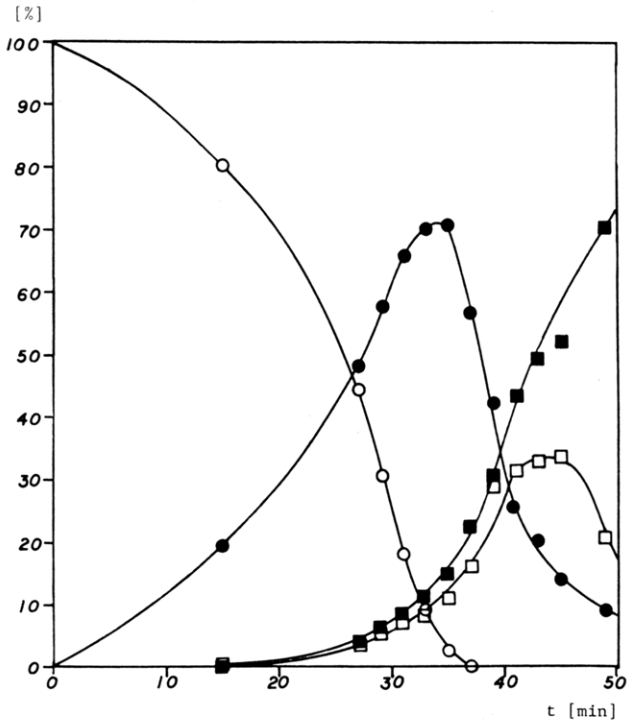

Figure 1. Reaction profile of the hydrogenation of 2-hexyne on untreated $Pd/CaCO_3$: ○ = 2-hexyne; ● = *cis*-2-hexene; □ = *trans*-2-hexane; ■ = *n*-hexane.

lead pretreatments. The reactions were conducted under standard conditions (heptane, 1 atm of hydrogen, room temperature). The study of other additives like quinoline in conjunction with lead was not incorporated in this paper since the effect of quinoline on Pd/C and Pd foil has been addressed in earlier papers.[7,20]

The effect of lead treatments on various Pd catalysts is summarized in Table I. A $Pd/CaCO_3$ catalyst was prepared by following the procedure of Gutmann and Lindlar[4] and its maximum selectivity for *cis*-2-hexene was determined to be only 74% (see Table I) before the modifying treatment with the lead acetate solution. The reaction profile is shown in Figure 1. This untreated catalyst was examined by transmission electron microscopy. An illustrative microstructure of the catalyst is shown in Figure 2a. Most of the Pd particles are in the form of agglomerates. The corresponding selected area electron diffraction pattern in Figure 2b shows a random orientation of Pd particles on the $CaCO_3$ support (main lines correspond to Pd agglomerates whereas faint lines, marked by arrows, correspond to $CaCO_3$). The difference in microstructure of $CaCO_3$ and Pd particles (average size 80–100 Å) was resolved by high resolution electron micrographs from a region with Pd particles and $CaCO_3$ support. The lattice fringe spacing in Pd particles corresponds to (111) planes of periodicity 0.22 nm and in $CaCO_3$ particles corresponds to (111) planes of $CaCO_3$ (0.33 nm). Figure 3 shows one such example where lattice fringes due to the $CaCO_3$ support as well as Pd particles are visible. The catalyst consists of inhomogeneously dispersed palladium of small particle size and varying morphology. A surface area of 0.6 m^2/g points to a dispersion of 2%. The dispersion and irregular structure is in agreement with the poor selectivity observed. Another fresh $Pd/CaCO_3$ sample (selectivity ~60%) when reused after 2 months of storage under ambient conditions,

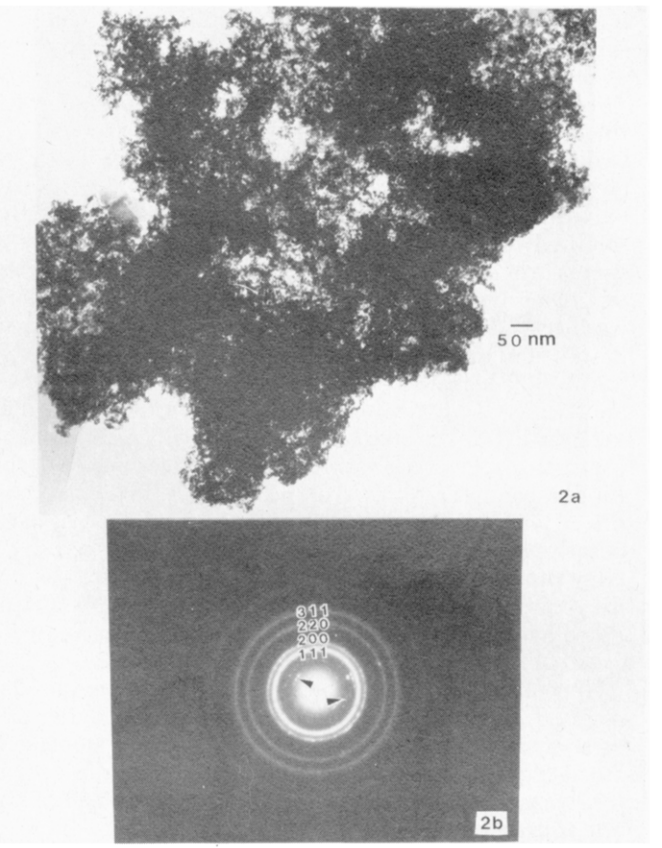

Figure 2. (a) Bright field electron micrograph of the fresh $Pd/CaCO_3$ catalyst. (b) Selected area electron-diffraction pattern corresponds to randomly oriented Pd particles. Some faint lines due to $CaCO_3$ support are marked by arrows.

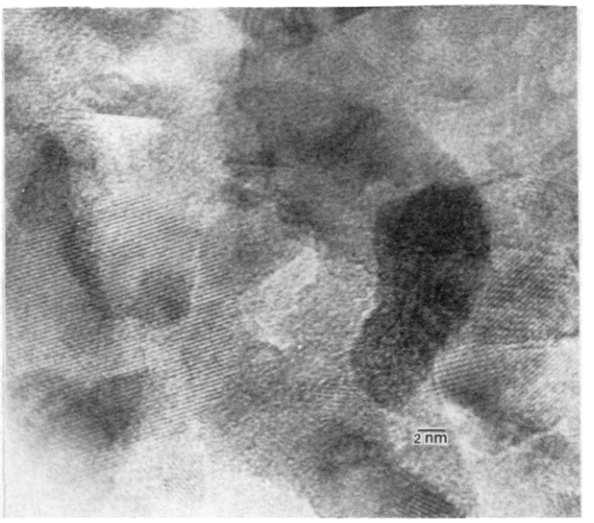

Figure 3. High resolution transmission electron micrograph of the fresh $Pd/CaCO_3$ catalyst. In some Pd particles lattice fringes are visible corresponding to the spacing of (111) planes. Also seen are fringes corresponding to the $CaCO_3$ support.

showed an increase in selectivity to almost 90%, indicating that some form of aging process improves the catalyst performance with time.

After the reflux treatment with lead acetate, the selectivity drastically increased from 74% to 91% (see Table I and the reaction profile in Figure 4). Transmission electron microscopy was then used to characterize the actual changes of this catalyst.

Upon treatment with lead acetate a change in morphology of the Pd catalyst was found. An example of the microstructure developed due to this treatment is shown

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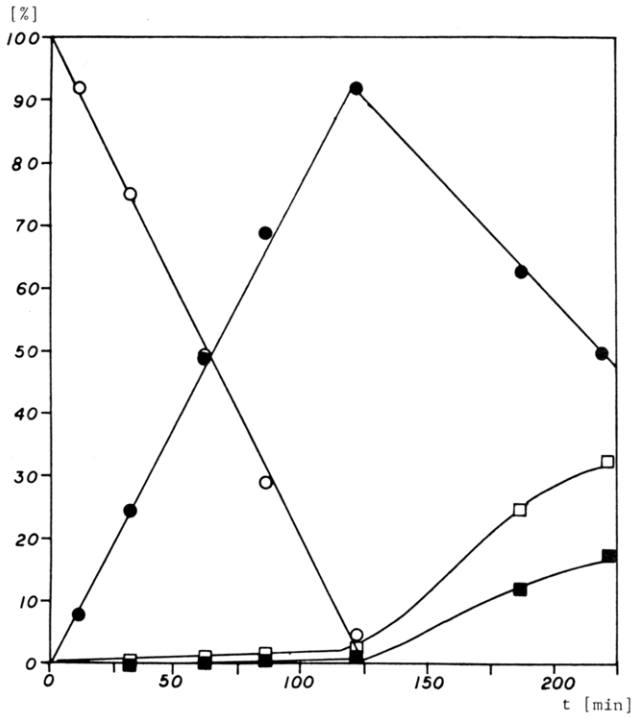


Figure 4. Reaction profile of the hydrogenation of 2-hexyne on $Pd/CaCO_3$ catalyst pretreated with lead acetate. Symbols are identical with Figure 1.

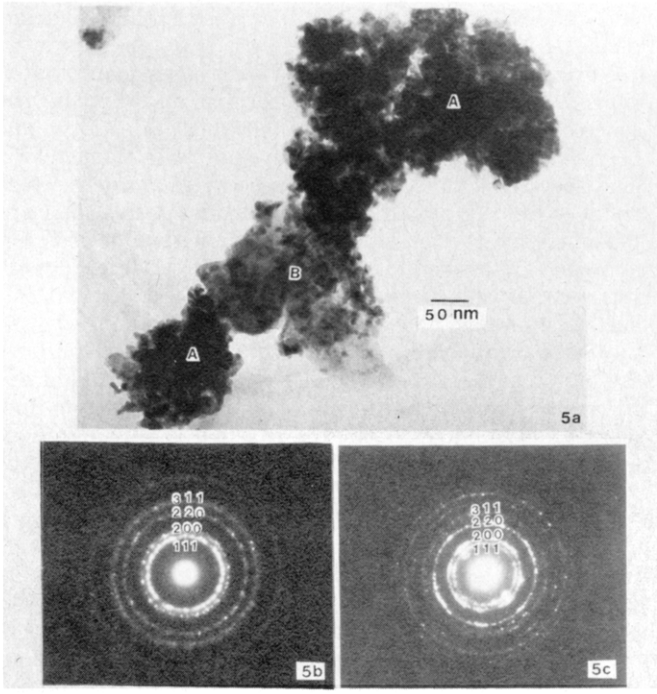


Figure 5. (a) Bright field electron micrographs of Pd catalyst pretreated with lead acetate on $CaCO_3$ support. Two types of regions are marked as A and B. (b) Selected area electron-diffraction pattern from type-A region. The diffraction pattern corresponds to randomly oriented Pd particles. (c) Selected area electron-diffraction pattern from the type-B region. The diffraction pattern corresponds to Pb particles in random orientations.

in Figure 5a. Two types of regions, i.e., A and B (marked in Figure 5a) can be noticed in this electron micrograph: 1. Region A shows a dense agglomeration of Pd particles on $CaCO_3$, but of larger size compared to the fresh catalyst (average size ~150–200 Å). Apart from Pd, a few overlapping Pb particles were also found. 2. Region B is

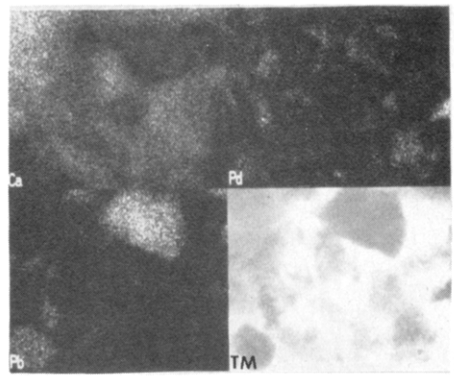


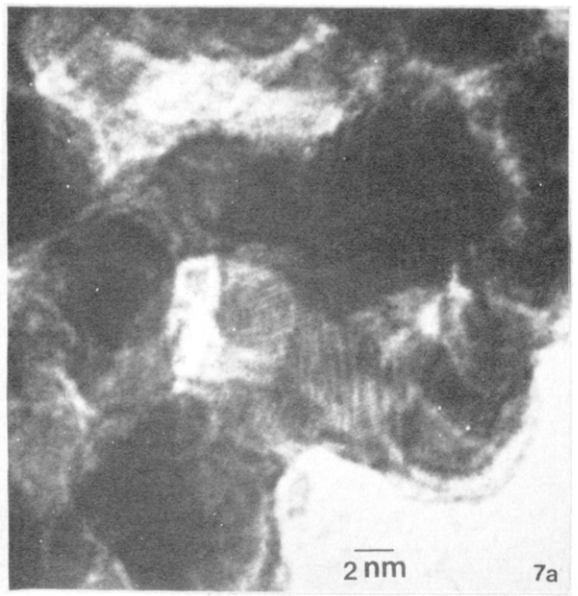
Figure 6. X-ray map showing the contrast due to Ca, Pd, and Pb particles and the STEM image of the catalyst.

dominated by Pb particles. Naturally, the selected area electron-diffraction patterns were different from the two regions. Selected area electron-diffraction from the A region (Figure 5b) corresponds mainly to Pd particles in random orientation, whereas from the B region it corresponds mainly to lead particles (Figure 5c) in random orientation.

X-ray mapping (in STEM mode) was employed to solve the question about the existence of lead containing Pd particles. This method, often referred to as X-ray microscopy, maps areas on the specimen by elements by recording the element specific X-ray emission. This allows one to determine the location and identification of elements of interest. In this case we were interested whether the lead deposition occurred exclusively on the Pd particles (in which case the images would be superimposed). The scanning transmission picture (Figure 6, lower right) shows the overall image of the selected area. The X-ray maps show the contrast due to Ca, Pd, and Pb particles as recorded on the same area. Careful inspection of Figure 6 confirms that there are only a few Pb particles overlapping with Pd particles while particles containing mainly Pd or mainly Pb alone are dominating.

High resolution electron micrographs were also taken from the two regions mentioned earlier. Figures 7a and 7b show the lattice fringe images from two regions. The fringe spacings of 0.22 nm and 0.28 nm correspond to (111) planes of Pd and Pb, respectively. Further energy-dispersive X-ray spectroscopy (EDXS) studies were also performed, particularly from the regions containing both Pd and Pb. No indication for the presence of Pd_3Pb alloy could be obtained, confirming Palczewska's results.[12] The TEM study clearly documents that a change in morphology of the Pd particles resulted from the lead acetate treatment. The lack of any dominant or uniform type of lead-containing Pd particles does not allow a meaningful correlation to be made between the lead deposition and the observed selectivity increase. However, poisoning of sites responsible for side reactions (steps and kinks) by lead deposition is not excluded by these results! That morphological changes brought about by the pretreatment can indeed result in a significant selectivity enhancement could be demonstrated with a commercial Pd/C catalyst. While the fresh Pd/C catalyst (see table) had a selectivity of only 77% for the formation of *cis*-2-hexene, pretreatment of the catalyst at 400 °C in H_2 (known to cause a decrease in dispersion of the Pd particles on carbon support[7]) resulted in a selectivity increase to 90%, comparable to that of the Lindlar catalyst.

The reaction profile of a commercial Lindlar catalyst was determined (Table I) to confirm that our synthesized Lindlar catalyst was indeed comparable to a commonly



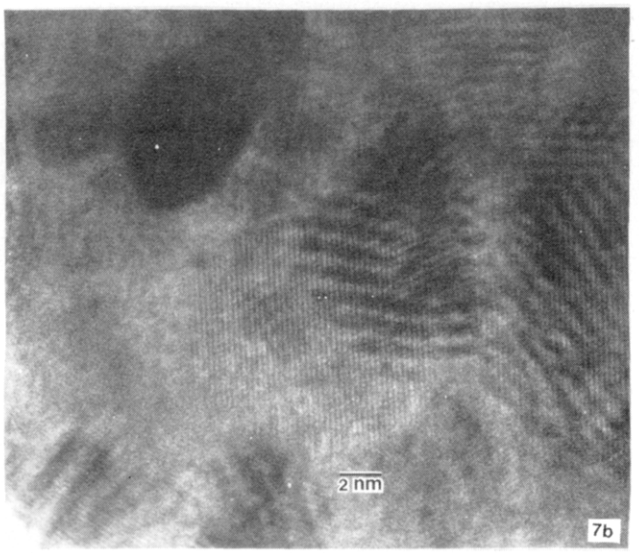


Figure 7. (a) High resolution electron micrograph showing the Pd agglomorates. In some Pd particles lattice fringes corresponding to (111) planes ($d \sim 0.22$ nm) are visible. (b) High resolution electron micrograph from B-type regions of Figure 5a. Lattice fringes in some Pd particles are clearly seen. The lattice fringe spacing corresponds to (111) planes of Pb.

used catalyst. The obtained selectivity of only 80% showed that our catalyst was more selective than the commercial one.

The β-hydride phase of Pd is known to be highly selective for alkyne hydrogenations.[16,21,22] It was therefore of interest to determine the propensity for the formation of the β-hydride phase of the catalysts under our reaction conditions. For bulk Pd foil we obtained a H/Pd ratio of 0.68 after 100 min, which compares well to a ratio of about 0.6 reported by others.[22] The 5% $Pd/CaCO_3$ did not absorb hydrogen into its bulk readily even when exposed to 800 mbar of hydrogen at room temperature. After 130 min the H/Pd ratio was only 0.06. However, hydrogen absorption continues slowly and after 7 h a H/Pd ratio of 0.48 was obtained, indicating slow β-hydride formation.

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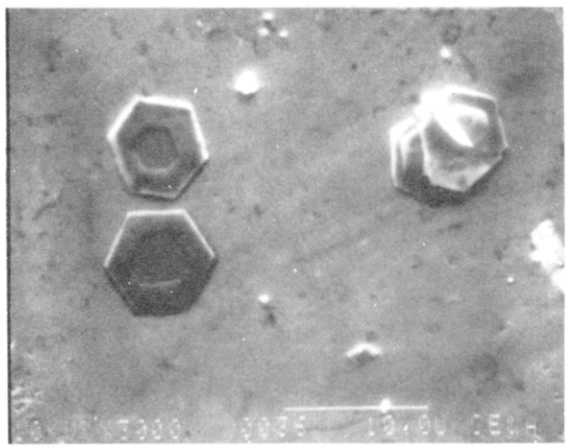

Figure 8. Low resolution scanning electron microscopy picture of $Pb(OAc)_2$ crystals on Pd foil formed during the Lindlar treatment.

The lead-treated $Pd/CaCO_3$ catalyst absorbed hydrogen into its bulk at a faster rate than the untreated 5% $Pd/CaCO_3$ catalyst but still not as fast as bulk Pd foil (after 100 min the H/Pd ratio was 0.25). Hydrogen absorption for 7 h resulted in a final H/Pd ratio of 0.40. This resulted H/Pd ratio of the Lindlar catalyst is in agreement with the ratio of 0.40 reported by Palczewska for the Lindlar catalyst.[12] The decreased propensity of the $Pd/CaCO_3$ catalysts to form β-hydride together with the rapid overhydrogenation after alkyne consumption (see Figures 1 and 4) does not support any importance of the β-hydride phase.

Various Pd foils were exposed to pretreatment conditions to characterize the effect lead has on Pd in the absence of support. A piece of Pd foil whose selectivity had been decreased to 74% by extensive use[16] was treated with lead acetate. The treatment caused an increase in selectivity to 88%, which indicates that unselective sites are poisoned by the pretreatment (deposition of lead on stepped and kinked sites?). New Pd foil, which has an intrinsic cis selectivity of 90%, was treated with lead acetate solution. The observed drop in selectivity to 82% indicates no special selectivity enhancement of the lead acetate pretreatment on a selective catalyst.[23] In addition, the more than 10-fold drop in reaction rate confirms that lead is a poison for the hydrogenation of alkynes. Low resolution electron microscopy pictures of the surface revealed the formation of crystallites of a very regular hexagonal symmetry (see Figure 8). Auger electron spectroscopy (AES) confirmed that these crystals contained lead, carbon, and oxygen, supporting their $Pb(OAc)_2$ nature. On the exposed areas of Pd no lead was detectable by AES. This indicates that lead is not deposited on low energy surfaces by the Lindlar treatment and seems to affect only the rough surface of Pd particles. Other methods of deposition were explored, to obtain the desired information on the effect of lead on Pd; electrochemical plating was found most suitable for monolayer deposition and thin film coating for the deposition of thicker films.

During the electrochemical lead deposition on new Pd foil (total surface) the beginning of the large cathodic peak was shifted from approximately 0 to −0.15 V (SCE), indicating that hydrogen evolution had been suppressed to some extent and lead was being plated onto the foil. The presence of lead together with Pd was confirmed by Auger

(23) Oxidation of the foil treated with lead acetate caused a complete loss of selectivity (50%) while the activity raised to a N_f of 1.2, indicating that indeed Pb(0) and not Pb(2+) is the form of lead in Lindlar catalysts.

spectroscopy, indicating that significant amounts had been deposited (Pb 94 eV/Pd 330 eV ~ 2:1). The depth profile with slow sputtering rate (approximately 2–10 Å/min) showed pure Pd after only 4 min, confirming a thin overlayer of lead. A low resolution electron micrograph of the surface confirmed homogeneity of the surface, contrasting the above foil after lead acetate treatment. Hydrogenation of 2-hexyne on this lead-plated Pd foil resulted in a selectivity decrease to 80% and a rate reduction to N_f = 0.2 (see also Table I), supporting the contention that lead acts mainly as a mild poison for the reaction.

The electrochemically treated Pb foil was also titrated with hydrogen. Again hydrogen migration into the bulk metal was observed. The hydrogen uptake (H/Pd = 0.68) was very similar to that of Pd foil alone, indicating that the lead deposition does not inhibit hydrogen absorption. This appears to contradict earlier results, which claim complete suppression of the hydrogen uptake after only 0.3 monolayer of lead.[11] Bulk lead was deposited on Pd foil by electrochemical plating to test for poisoning effects of lead. This foil (N_f 0.3) showed an activity similar to the Pd foil with a thin layer of lead; however, a drop in selectivity to 68% was noted. To confirm this result new Pd foil was coated with 300 Å of lead by evaporation in a film deposition chamber. 2-Hexyne hydrogenation on this lead-covered Pd foil resulted in a similar reaction profile as obtained on the Pd foil with electrochemical lead deposition. Again, no Pd was exposed (as confirmed by Auger electron spectroscopy), indicating that the hydrogenation must have occurred on the lead overlayer. The low selectivity confirms that a lead overlayer by itself cannot be responsible for any selectivity increase.

This study reveals that the lead acetate treatment enhances the selectivity of the catalyst in part by the rearrangement of Pd particles. Such rearrangements are likely to be affected by many factors other than the lead acetate. A fresh $Pd/CaCO_3$ catalyst was pretreated with NaOAc instead of $Pb(OAc)_2$ to test whether the lead contributes at all in the pretreatment procedures. No change in selectivity confirms that lead is essential for the observed selectivity increase after the Lindlar treatment.

Conclusion

No evidence for the formation of selectivity enhancing lead–palladium alloys or lead-containing surface compounds was obtained. The selectivity increase obtained in the absence of quinoline or other additives is most likely due to the morphological rearrangement that the catalyst undergoes during the lead acetate treatment. Indications of selective poisoning of unselective sites (steps and kinks) were obtained but could not be characterized by the applied techniques. The selectivity enhancing action of the Lindlar treatment seems to be the increase of terrace type Pd surface atoms relative to stepped and kinked sites.

The much simpler and more effective use of additives like quinoline, the formation of more selective catalysts by thin film deposition techniques, or the use of the more selective Pd_3Pb alloy do not seem to merit further pursuit of the lead treatments for catalyst modifications.

Experimental Section

Chemicals were obtained commercially and used without further purification. The commercial Lindlar catalyst was obtained from Aldrich. Ultrapure water was used in all electrochemical experiments, preparation of supported catalysts, and lead acetate pretreatments. The hydrogenations were monitored with a HP5890A gas chromatograph equipped with a capillary column (60-m SPB-1 from SUPELCO) and FID detector. Extent of reaction and product compositions were obtained from integration of the GC peaks by a Hewlett-Packard 3390A integrator and are uncorrected GC area %. The products of hydrogenation were identified by coinjection with authentic samples.

For calculation of the turnover frequency, N_f, the rate of loss of alkyne for the initial 50% of reaction was used. The surface area of the foils was taken to be their total geometric surface area; when lead was present no correction was made for the loss in total surface area. The surface area of the supported catalysts was calculated from the dispersion measurements. The number of active sites was calculated from these surface areas and the assumption that there are 1.4×10^{15} surface atoms/cm^2 of metal surface.

$Pd/CaCO_3$. The $CaCO_3$ was precipitated from equimolar solutions of $CaCl_2$ and Na_2CO_3, washed with copious amounts of ultrapure water, and dried at 100 °C overnight before use. The 5% $Pd/CaCO_3$ was prepared from 479 mg of $PdCl_2$ and 6.13 g of $CaCO_3$ by using the standard Lindlar procedure but stopping before the lead acetate treatment stage.[4]

$Pd/CaCO_3$ Pretreatments. (1) $Pd/CaCO_3$ (5%) (1.92 g) was heated at 75–85 °C for 45 min, filtered, and washed with ultrapure water. The catalyst was dried overnight at 100 °C in an oven before use. (2) A sample of 327 mg of $PdCl_2$ was added to 3.6 g of $CaCO_3$ by using the standard Lindlar procedure and in this case the catalyst was taken all the way through the lead treatment stage. The final weight of the catalyst was 2.3 g, the loss was assumed to be $CaCO_3$, and from this value a final loading of 8% was calculated.

Pd Foil. Commercial Pd foil was used without pretreatment. For the lead acetate pretreatment some foil that had been used extensively for hydrogenations of 2-hexyne was used. This foil had been exposed to high temperature oxygen and nitrogen pretreatments.[16]

Pretreatment of Pd/C Catalyst. Pd/C catalyst (Aldrich) (10%) (4.082 g) dried in H_2 at 138 °C for 24 h and used to determine the selectivity for 2-hexyne hydrogenation; 1.25 g of this catalyst was heated for an additional 4 h in H_2 at 406 °C. The dispersions of these catalysts were determined to 13% and 6%, respectively.

Pd Foil Treatments. (1) A sample of 112 mg of unused Pd foil was heated in a solution consisting of 6 mL of 7.7% lead acetate diluted with 30 mL of water for 45 min at 75–85 °C. The solution was filtered and the catalyst rinsed thoroughly with water and dried overnight at 100 °C. (2) A sample of 500 mg of extensively used Pd foil was heated for 40 min in a solution consisting of 3.6 mL of 7.7% lead acetate diluted with 12 mL water at 75–85 °C. The foil was filtered, rinsed thoroughly and dried overnight at 100 °C.

Lead Coating of Pd Foil. New Pd foil was glow discharged on both sides in a vacuum chamber (Balzers, BAE-080) at 8×10^{-1} mbar for 10 min. At a substrate temperature of 240 °C and a pressure of 5×10^{-6} mbar Pb was evaporated with an e-gun (deposition rate ~30 Å/min). The deposition was monitored with a quartz crystal thickness monitor.

Electrochemistry Studies. Electrochemical pretreatments were carried out at 25 °C in 1 M $HClO_4$. The solutions were deoxygenated with nitrogen prior to use. The reference electrode was a saturated calomel electrode (SCE) separated from the working electrode via a reference electrode bridge tube equipped with a Vycor frit and filled with 1 M $HClO_4$. All potentials refer to the SCE. Potentials were controlled with an EG&G Model 362 scanning potentiostat. Voltamograms were recorded on an Omega RD 200 XY recorder. (1) The electrochemical plating of lead on Pd foil began with repeated cycling of 87 mg of foil in 1 M $HClO_4$ at potentials between 1.0 and 0.0 V (SCE) at 20 mV/s until a reproducible CV was obtained. The solution was then replaced with 1×10^{-3} M $Pb(ClO_4)_2$ in 1 M $HClO_4$ and the foil cycled once completely from 1.0 to −0.2 V (SCE) and then brought to −0.2 V at 20 mV/s when the circuit was broken and the foil removed from the solution. (2) The same treatment was applied to 113 mg of unused Pd foil except that the concentration of lead was increased to 0.1 M and the potential for plating lowered to −0.50 V (SCE) and held for 2 min.

Surface Area Determinations. The dispersions of the 5% $Pd/CaCO_3$ catalyst before lead pretreatment and the 8% Pd/$CaCO_3$ catalyst after lead pretreatment were obtained by deu-

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.

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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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