The phenyl migration occurs under aerobic conditions in protein systems, and we have made some observations relevant to the involvement of dioxygen in that process. Addition of limited amounts of dioxygen to **1** in chloroform-*d* at −60 °C results in the formation of both **2** and **3**. Thus, dioxygen is fully capable of effecting the iron(III) to iron(IV) oxidation required in eq 1.

## Experimental Section

**Materials.** Dioxygen was removed from chloroform-*d* by three freeze–pump–thaw cycles, and the solvent was placed in a Vacuum Atmospheres glovebox under an argon atmosphere and stored over 4-Å molecular sieves. Phenylmagnesium bromide and *p*-tolylmagnesium bromide were purchased from Aldrich Chemical Co. and Alfa. Phenyl-$d_5$-magnesium bromide and *m*-tolylmagnesium bromide were synthesized by using standard procedures. The iron(III)-phenyl complexes were prepared from the appropriate porphyrin and Grignard reagent by using an established procedure.[5] Pyrrole-deuterated $(TPP)H_2$ was prepared according to a standard procedure.[50]

**Oxidation of 1.** A chloroform solution of **1** was prepared under an argon atmosphere, placed into an NMR tube, sealed using a rubber septum cap, and wrapped with parafilm. In a typical experiment, a 3 mM solution of **1** was cooled to −60 °C and titrated with a bromine/chloroform solution (via a syringe). The sample was gently shaken and its color changed from light to dark red. The progress of the reaction was followed by NMR spectroscopy.

**Magnetic Susceptibility Measurement.** The solution magnetic measurements were made at −60 °C by using the Evans' method[51] with tetramethylsilane as the reference. The sample purity was confirmed before and after the measurements were made. The iron porphyrin concentration was determined by UV–vis spectroscopy after the sample was warmed to room temperature by converting it to (TPF)FeCl through treatment with gaseous hydrogen chloride. The original sample of **2** (R = $CH_3$, X = Br, and A = $C_6H_5$) contained 13% (TPP)FeCl and (TPP)FeBr as determined from the NMR spectrum. The magnetic susceptibility (after correction for the iron(III) impurity with an assumed susceptibility of 5.9 $\mu_B$) was 2.6 ± 0.4 $\mu_B$ for **2**.

**Instrumentation.** NMR spectra were obtained on Nicolet NT-360 FT and NM-500 spectrometers operating in the quadrature mode ($^1H$ frequencies are 360 and 500 MHz, respectively). Between 200 and 1000 transients were accumulated over a 40-kHz bandwidth with 16K data points for $^1H$ (4–8K for $^2H$) and a 6-$\mu$s 90° pulse. The signal-to-noise ratio was improved by apodization of the free induction decay which introduced a negligible 3–10-Hz line broadening. The peaks were referenced against tetramethylsilane. Electronic spectra were measured with a Hewlett-Packard 8450 A spectrophotometer.

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**Registry No. 1** (R = H; A = *p*-$C_6H_4CH_3$), 87607-84-9; **1** (R = D; A = $C_6H_5$), 101248-90-2; **2** (R = H; X = Br; A = $C_6H_5$), 101248-78-6; **2** (R = *p*-$CH_3$; X = Br; A = $C_6H_5$), 101248-79-7; **2** (R = *m*-$CH_3$; X = Br; A = $C_6H_5$), 101248-80-0; **2** (R = *p*-$CH_3$; X = $ClO_4$; A = $C_6H_5$), 101248-81-1; **2** (R = *m*-$CH_3$; X = $ClO_4$; A = $C_6H_5$), 101315-90-6; **2** (R = *p*-$CH_3$; X = $SbF_6$; A = $C_6H_5$), 101248-83-3; **2** (R = H; X = Br; A = *p*-$CH_3C_6H_4$), 101248-86-6; **2** (R = H; X = $ClO_4$; A = *p*-$CH_3C_6H_4$), 101248-87-7; **2** (R = D; X = $ClO_4$; A = $C_6H_5$), 101248-91-3; **3** (R = *p*-$CH_3$; X = $ClO_4$; A = $C_6H_5$), 101248-92-4; [*p*-$CH_3C_6H_4Fe^{IV}$(TPP)-Py]$ClO_4$, 101248-85-5; $(CH_3O)_2Fe^{IV}$(TMP), 101248-88-8; $Fe^{III}$-(TPP·)$(ClO_4)_2$, 83435-87-4; $(Im)_2Fe^{III}(TPP\cdot)^{2+}$, 101248-89-9; $(CN)_2$-$Mn^{III}(TPP)^-$, 93383-76-7; $(Im)_2Mn^{III}(TPP)^-$, 75120-59-1; $Br_2$, 7726-95-6.

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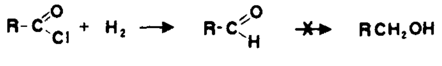
# Metamorphosis of Palladium and Its Relation to Selectivity in the Rosenmund Reaction

**Wilhelm F. Maier,*[†] Susan J. Chettle,[†] Raghaw S. Rai,[‡] and Gareth Thomas[‡]**

*Contribution from the Department of Chemistry and the Department of Materials Science and Mineral Engineering, University of California, Berkeley, California 94720, and the Center for Advanced Materials and the National Center for Electron Microscopy, Materials and Molecular Research Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720.* *Received June 13, 1985*

**Abstract:** Drastic changes in morphology and particle sizes of the Pd particles were detected during the classical catalyst pretreatment. These changes are connected to the increase in selectivity as well as to the problems encountered in the Rosenmund reaction. A major action of the poison in Rosenmund reactions was found to be the acceleration of the initial reconstruction of the surface of fresh catalysts to prevent overreduction. The instability of the Pd under reaction conditions appears to be responsible for typical problems encountered with the Rosenmund reaction such as irreproducibility and catalyst deactivation during the reaction. With the use of Pd single crystals stepped and kinked surfaces were found to be active for the hydrogenolysis of acid chlorides to aldehydes. Transmission electron microscopy and diffraction have been employed to characterize the change in dispersion and structure of Pd particles on carbon supports after various pretreatments.

The reduction of acid chlorides discovered by Sayzeff in 1872[1] and exploited by Rosenmund,[1b] was for a long time the only useful method to convert carboxylic acids and derivatives into the corresponding aldehyde. The reaction is based on a supported Pd catalyst and special reaction conditions had been developed to prevent the undesired overreduction.



$$R-C(=O)Cl + H_2 \longrightarrow R-C(=O)H \not\longrightarrow RCH_2OH$$

It has been found that the reduction of the aldehyde formed can be prevented by the use of suitable catalyst "poisons", "modifiers", or "regulators" which deactivate the catalyst selectively. Much attention has been paid to the development of such regulators,[2] which consist of quinoline with sulfur,[3] pyridine and copper,[4] thiophen or thiourea,[5] dimethylaniline,[6] ethyldiiso-

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[†] Department of Chemistry and the Center for Advanced Materials.

[‡] Department of Materials Science and Mineral Engineering and the National Center for Electron Microscopy.

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propylamine,[7] sodium acetate,[8] and 2,6-dimethylpyridine.[9] However, it was also shown with aliphatic as well as with aromatic substrates that the use of a regulator is not always necessary.[2,10]

It has been demonstrated that the overreduction to the alcohol is a stepwise process.[5] The involvement of a ketene intermediate as precursor in the reduction of aliphatic acid chlorides has been excluded by the formation of the monodeuterio aldehyde from acid chloride, indicating a simple C–Cl bond hydrogenolysis.[7]

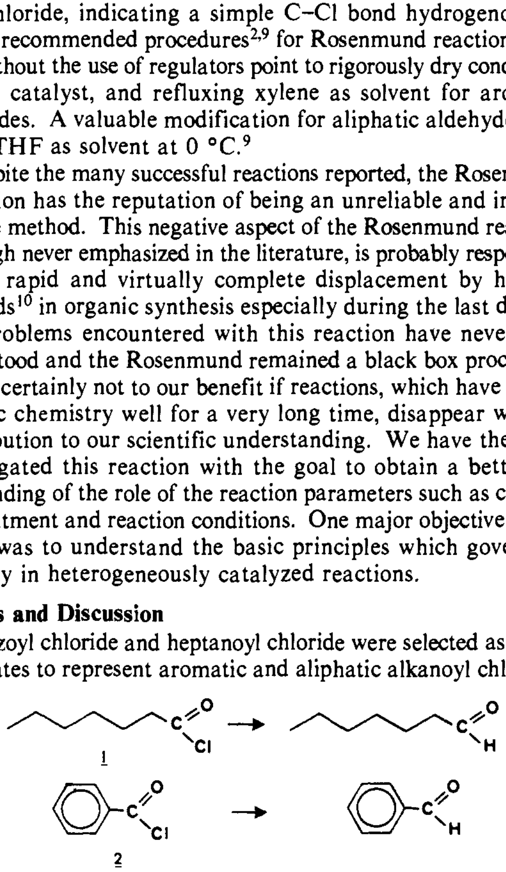
The recommended procedures[2,9] for Rosenmund reactions with and without the use of regulators point to rigorously dry conditions, 5–10% catalyst, and refluxing xylene as solvent for aromatic aldehydes. A valuable modification for aliphatic aldehydes employs THF as solvent at 0 °C.[9]

Despite the many successful reactions reported, the Rosenmund reduction has the reputation of being an unreliable and irreproducible method. This negative aspect of the Rosenmund reaction, although never emphasized in the literature, is probably responsible for its rapid and virtually complete displacement by hydride methods[10] in organic synthesis especially during the last decade. The problems encountered with this reaction have never been understood and the Rosenmund remained a black box procedure.

It is certainly not to our benefit if reactions, which have served organic chemistry well for a very long time, disappear without contribution to our scientific understanding. We have therefore investigated this reaction with the goal to obtain a better understanding of the role of the reaction parameters such as catalyst pretreatment and reaction conditions. One major objective in this study was to understand the basic principles which govern selectivity in heterogeneously catalyzed reactions.

## Results and Discussion

Benzoyl chloride and heptanoyl chloride were selected as model substrates to represent aromatic and aliphatic alkanoyl chlorides.



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We found that the acid chloride preparation is of crucial importance for reproducible results. Oxalyl chloride appeared to be the reagent of choice; alkanoyl chlorides prepared with thionyl or phosphorus oxychloride were found to show a strong tendency to cause rapid catalyst deactivation (probably due to remaining reagent traces in the distilled alkanoyl chloride). Kinetic studies, which have rarely been as conclusive in heterogeneous catalysis as in homogeneous organic reactions, rely on the catalyst as being constant during reaction conditions. However, initial observations about the structural rearrangement of Pd/alumina and Pd black catalysts in the presence of amines[11] present strong evidence for an unusually labile catalyst system which ruled out any straightforward kinetic relationship. If indeed structural rearrangements of the catalyst metal were initiated by organic substrates its relation to the reaction of interest had to be investigated. Rather than studying the effect of the catalyst on the organic substrate an investigation about the effect of reaction conditions and organic substrates on the catalyst was carried out. During our studies under proper reaction conditions we usually observed quantitative conversion to the aldehyde. The only important side reaction observed was the formation of the associated alcohol. Since quantitative conversions of heptanoyl chloride and benzoyl chloride are no special achievement with Rosenmund catalysts we will not comment further on yields and conversions.

**Table I.** Metal Surface Area of Pd Catalysts after Various Catalyst Treatments [$m^2/g$]

| catalyst | fresh | xylene refl. 4 h | xylene refl. 4 h quinoline sulfur | room temperature[a] 20 h |
|---|---|---|---|---|
| 10% Pd/C | 9.5 | 2.0 | 0.6 | 3.5 |
| 5% Pd/$BaSO_4$ | 6.7 | 1.3 | 0.7[b] | |

[a] Reaction with heptanoyl chloride in cyclopentane in the absence of modifiers. [b] After $O_2$ treatment. The refluxed catalyst was oxidized in pure $O_2$ at 700 °C to remove carbonaceous layers.

**1. Catalyst Stability.** The rate of a catalytic reaction should be proportional to the number of active sites on the surface and thus proportional to the total number of metal surface atoms. The determination of the metal surface area of a catalyst is therefore an important factor which characterizes the catalyst employed. The determination of Pd surface areas by $H_2$ adsorption methods is aggravated by the metal's unique ability to dissolve hydrogen to form the $\beta$-hydride phase, especially at lower temperatures[12] and pressures above 2 kPa.[13] We have therefore employed the $H_2/O_2$ surface area titration method,[14] shown to give reliable results at low partial pressures of hydrogen,[15] to examine the change in metal surface area of supported Pd catalysts. No attempts were made to correct or calibrate the surface areas determined, since only their relative change is of importance for this investigation. The results are summarized in Table I.

The Pd surface of 9.5 $m^2/g$ on a fresh 10% Pd/C catalyst covers only about 2% of the total carbon surface available (500 $m^2/g$ determined by the BET method[16]). Clearly, most of the carbon surface is not occupied by the Pd and thus may act as charcoal to adsorb organic substrate and to carry undesired materials such as water into the reaction. Such support bound water is probably the source for undesired side reactions such as anhydride formation and calls for a thorough predrying of the catalyst employed.

More surprising is the effect of pretreatment and reaction conditions on the Pd itself. A drastic change in surface area (see Table I) of the catalyst under all conditions investigated indicates fast rearrangements of the Pd metal on the carbon support indicative for a weak metal support interaction.[17] Reflux in xylene for 4 h under $H_2$ results in a reduction of the metal surface area by over 75%. This surface loss is accelerated by the presence of traces of the usual modifiers, quinoline and sulfur, which increased the loss of metal surface to 90% relative to the fresh catalyst (4 h reflux in xylene in the presence of quinoline and sulfur). Even under mild reaction conditions (room temperature, 5% heptanoyl chloride, cyclopentane) a loss of metal surface by 60% is observed. To exclude a possible surface coverage by carbon (continuous deactivation of the catalyst by carbonation), xylene, or modifiers, a similar study on a 5% Pd/$BaSO_4$ catalyst was performed. Although $BaSO_4$ is a crystalline material which does not have the large surface area of the amorphous classical supports like carbon, silica, or alumina, the total metal surface area of the fresh catalyst was similar to that of the carbon catalyst. The rearrangement of the Pd on $BaSO_4$ appeared to be more efficient than on carbon as indicated by the xylene reflux experiment where a total re-

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Table II. Formation of Alcohols from Aldehydes Formed during Rosenmund Reduction of Acid Chlorides with Various Pretreated Pd Catalysts

| expt | catalyst | heptanol | benzyl alcohol |
|---|---|---|---|
| 1 | Pd/C fresh | yes | yes |
| 2 | Pd/C xylene refl. | no | yes, but slow |
| 3 | Pd/C xylene refl. + quinoline + sulfur | no | no |
| 4 | Pd/C fresh + quinoline at RT | no | no, very slow reaction |
| 5 | Pd/C r.t. reaction | no | no |
| 6 | Pd/C heated to 1000 °C | no | no |

duction of the metal surface of 95% was achieved (see Table I). This apparently weaker metal support interaction may be the origin for empirical results which claim $BaSO_4$ a superior support for the Rosenmund reaction relative to carbon.[1b,18] Subsequent oxidation of this catalyst in pure oxygen at 700 °C did not produce the increase in surface area expected from a carbonated surface but resulted in a further loss of the metal surface area. In agreement with our earlier studies, where carbon was hardly detectable by elemental analysis on the deactivated catalyst,[11] carbonation or surface coverage by solvent or modifiers does not appear to be responsible for the observed change in metal surface area.

The results indicate that Pd is a very labile catalyst whose particle size and surface structure change rapidly under reaction conditions, especially during the initial use of the fresh catalyst. The loss of surface area observed could be confirmed by transmission electron microscopy studies, where a drastic change in Pd particle size and morphology of the catalysts (see below) confirmed the observed loss of Pd surface. With order of magnitude changes in the active metal surface area all morphological forms of the catalyst become possible and the formation of specific active sites (certain surface structures or particle sizes etc.) during the initial metal rearrangements had to be considered as the possible origin for the selectivity observed. This morphological change of the catalyst complicates any mechanistic study because it seems impossible to determine the partitioning of observed effects on reaction rate or selectivity between classical parameters like solvent polarity or temperature and surface effects of the catalyst metal due to the rearrangement processes. In order to obtain a global picture of the reaction it became crucial to analyze the reaction for both: the more classical reaction parameters like the effect of modifiers, substrate, and solvent by standard methods and the active site requirements with the help of single crystal surfaces. The most significant results of these studies are summarized in the following sections.

**2. Role of Modifiers.** One action of modifiers found, which is to compete with the substrates for surface interaction and thus reduces the overall reaction rate, has been recognized before.[4,5,7,17] The other action of the modifiers appears to be the acceleration of the surface reconstruction of a fresh catalyst (see Table I). Since we achieved reproducibility of the surface area determinations within 5%, the observed difference in surface area of the xylene refluxed catalysts in the presence and absence of the modifiers must be attributed to enhanced rearrangements in the presence of the quinoline. A similar but more drastic observation has already been made in our earlier report when Pd black rearranged to metallic Pd in the presence of triethylamine at 150 °C.

Table II and Figure 1 summarize the effect of various catalyst pretreatments and reaction conditions on the reaction rate and selectivity. Fresh Pd/C catalyst in the absence of any modifier causes over-hydrogenation of the aromatic and aliphatic aldehydes (experiment 1, Table II). Reflux treatment of the catalyst in xylene is sufficient to make the catalyst inert for aliphatic aldehyde reductions but some activity for aromatic aldehyde reduction is preserved (experiment 2). The presence of the classical modifier quinoline/S during catalyst pretreatment (experiment 3) achieves the desired selectivity toward aliphatic and aromatic aldehydes. Even a fresh Pd/C catalyst is selective if quinoline is added to the reaction mixture (experiment 4), indicating that added modifiers compete successfully with the aldehyde formed for surface interaction on the Pd.

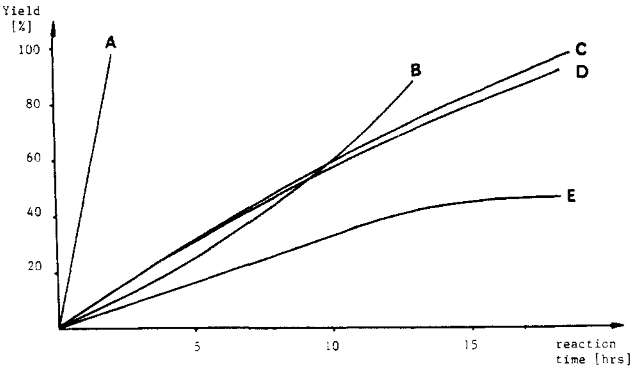

**Figure 1.** Formation of benzaldehyde from benzoyl chloride with various pretreated catalysts; reactions carried out under the following pretreatment conditions: (A) catalyst refluxed in octane, (B) catalyst refluxed in xylene with sulfur, (C) catalyst refluxed in xylene with quinoline and sulfur, (D) catalyst refluxed in xylene with quinoline, and (E) catalyst refluxed in xylene.

In experiment 5 the catalyst had been used once already in a 20 h room temperature reaction of heptanoyl chloride with hydrogen in cyclopentane as a solvent (alcohol and aldehyde formation were observed initially as expected from a fresh Pd/C). This used catalyst, which had never been in contact with any added modifier, showed absolute selectivity toward aldehyde formation from the aliphatic and aromatic substrate which points to a catalytic self-modification effect during the reaction (probably caused by the substrate and/or the products). We also saw exclusive aldehyde formation from benzoyl chloride in various experiments with xylene reflux (7 h) as well as *n*-octane pretreated catalysts (experiments D and A from Figure 1). This together with the many literature reports[2] shows that additional modifiers are not required to achieve the desired Rosenmund selectivity. It appears that modifiers rather supplement the catalytic selectivity by accelerating the catalyst rearrangement and successful surface competition with the aldehyde formed. Fresh catalysts, which are in an inselective stage due to incomplete morphological changes, greatly benefit from the presence of such surface competition whereas with a catalyst in a selective stage added modifiers mainly reduce the overall rate. At this point we can only speculate that small Pd particles (see Figure 2), present on the relatively highly dispersed, fresh Pd/C catalyst, are responsible for the overhydrogenation activity.

In experiment 6 a fresh Pd/C catalyst was heated to 1000 °C in hydrogen for 4 h and was found to be completely inactive for acid chloride and aldehyde reduction. This amplifies the effect of continuing Pd rearrangements which eventually lead to a complete deactivation not so much by poisoning but rather by a loss in active metal surface area through the formation of large metal particles (see electron microscopy studies below).

The action of the hydrogen chloride formed during the reaction on the reduction of the aldehydes was studied in parallel experiments with fresh Pd/C in the presence and absence of HCl gas. It was found that HCl successfully prevents the reduction of the aliphatic aldehyde and reduces the rate of benzaldehyde reduction by a factor of 10. Therefore we have to consider the HCl formed as a modifier which can increase the overall selectivity of the reaction. Although we have not observed aldol condensation under our conditions, the potential catalytic effect of HCl for this side reaction has already resulted in various modifications of the reaction conditions.[7-9]

Figure 1 shows the effect of various changes of the reaction environment on the reaction rate. All reactions were conducted under as identical conditions as possible. The interpretation of this scheme, however, has to be cautious because it has not been

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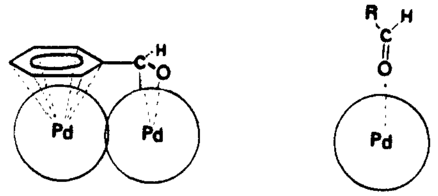
**Scheme I.** Proposed Difference in Surface Interactions of Aromatic and Aliphatic Aldehydes



corrected for the morphological changes the catalyst experienced during these reactions. Most drastic is the fast reaction rate achieved with the *n*-octane (A) relative to xylene (E) as a solvent in the absence of any modifier. This points to successful surface competition of the xylene through its aromatic $\pi$-system resulting in an overall rate reduction relative to the inert hydrocarbon *n*-octane. Interesting is the drop in activity after about 12 h of reaction E relative to reactions C and D which may indicate that the presence of modifiers reduces the continuing deactivation of the catalyst surface. Besides a 3% alcohol formation observed only in reaction B no special effect of sulfur on the reaction could be identified (reactions C and D are almost superimposible). Sulfur alone (compare B and E) appears to have a similar effect as the quinoline (compare D and E), but the reaction rate seems to increase with time. However, no further experiments to elaborate on these observations have been conducted.

**3. Role of Solvent.** The standard Rosenmund conditions employ refluxing xylene as reaction medium. Besides the empirical recommendations two advantages in such a solvent choice can be identified. The first and probably most important one is the high reflux temperature which, even in the absence of modifiers, helps to deactivate any fresh Pd catalyst by the rearrangement processes discussed above. Another advantage is that xylene allows for facile removal of water from catalyst and reaction environment by azeotropic distillation prior to the acid chloride addition.

Many spectroscopic studies on various surfaces have concluded that benzene chemisorbs on transition-metal surfaces with its ring parallel to the surface plane ($\pi$-interaction).[19] In analogy we conclude that xylene will behave accordingly. From the sensitivity of the reaction to surface competition xylene should be a poor choice with respect to the overall reaction rate since it may compete with the substrate for free active sites (coordination sites) on the catalyst surface with its aromatic $\pi$-system. Such a hypothesis is supported by the tenfold increase in reaction rate (see Figure 1) with *n*-octane (Kp 126 °C) compared to the reaction in refluxing xylene (Kp 137–140 °C) mentioned above.

**4. Role of Substrate.** The effect of substrate structure on the selectivity of the catalyst is evident from experiments 1 and 2 in Table II. Aromatic aldehydes are reduced more readily than aliphatic aldehydes. The lack of activity for aliphatic aldehyde reduction of the "deactivated" Pd catalyst must be due to a preferred lone pair interaction of the carbonyl oxygen to the Pd surface relative to the possible $\pi$-complex. The likely interaction of the $\pi$-system of an aromatic aldehyde (see Scheme I) with the surface may force the carbonyl group into a $\pi$-interaction with the surface, initiating the reduction process.

After exploring the interaction of additives, substrates, solvents, and catalysts the central problem to be addressed is to obtain some information on the active site and its relation to the Pd reconstruction processes that occur upon catalyst pretreatment.

**5. Active Site Study.** The key to understanding catalytic reactions is to accumulate knowledge about the active site. Since nothing is known about the active site of catalysts used in the Rosenmund reaction (and little about active site structures in general) we started the investigation with the reasonable hypothesis that the active site is found on the Pd particles of the catalyst. At first we obtained information on the oxidation state of "active" Pd. Since Pd is well known to reduce readily to Pd zero by exposure to hydrogen, a simple determination of the oxidation of the gross Pd surface by XPS (we measured a core binding energy of 335.22 eV on a $Pd/SiO_2$ catalyst which corresponds to Pd zero) is not likely to reveal reliable information about the oxidation state of the active site. $Pd^{II}$ or other higher oxidation states of the Pd, leftovers from incomplete reduction of the Pd compounds used for catalyst preparation or formed by simple air exposure of the catalyst, could be excluded readily as active sites by indirect methods. If surface oxidation is an important factor than preoxidation of a Pd catalyst should increase activity and prolonged reduction should decrease the reactivity of a catalyst. As indicated in Table III the experiments show the opposite effect—careful reduction of the catalyst prior to the experiment resulted in the most active catalyst (experiment 4, Table III). No enhancement of the activity was obtained by the preoxidation of Pd powder. Even the use of pure PdO or $PdCl_2$ as catalyst did not result in an enhanced activity. The low yields and selectivity obtained with such oxidized forms of Pd and the black Pd deposit formed during the reaction point to zero valent Pd as the catalytically active species. The investigation was therefore continued with a study on the nature of the active metallic Pd species.

**Table III.** Reaction of Heptanoyl Chloride with Hydrogen in the Presence of Various Forms of Pd

| expt | catalyst | pretreatment | heptanal | heptanol | rel. rate |
|---|---|---|---|---|---|
| 1 | Pd/C | none used | yes | yes | 1 |
| 2 | Pd/C | none used | yes | | 0.3 |
| 3 | Pd/C | $O_2$, 80 °C, 24 h | yes | | 0.5 |
| 4 | Pd/C | $H_2$, 180 °C, 24 h | yes | | 1 |
| 5 | PdO | | 3% | | |
| 6 | Pd powder | | yes | none | |
| 7 | Pd dust | | yes | none | |
| 8 | $PdCl_2$ | | yes | some | |
| 9 | Pd foil | | no activity | | |
| 10 | Pd foil | scratched | yes | | |
| 11 | Pd/C | $H_2$, 1000 °C, 4 h | no activity | | |

As has been found previously,[11] no reaction could be detected on Pd foil as a catalyst. After a reaction time of 7 days with **1** and with **2** under reflux in toluene no trace of aldehyde was detectable, indicating that the low energy surface on the Pd foil did not contain a sufficient concentration of the active sites. Assuming that Pd foil, as all solid metals, is composed of relatively large metal grains (>100 Å) we conclude that the dominant surface structure is composed equally of the low energy (100) and (111) terraces. This points to higher energy sites as the prerequisites for active sites. Higher energy sites may be characterized as all surface atoms with fewer direct neighbors than (111) (nine direct neighbor atoms) or (100) surface atoms (eight direct neighbors).[20] Such coordinatively less saturated surface atoms are found on small metal particles and at the end of a terrace (steps, 7 neighbors) and at a corner (kinks, 6 neighbors). In order to increase the relative number of more reactive atoms on a foil surface the foil was treated with a fine abrasive (increase the roughness), and indeed with the rough Pd foil heptanal formation from heptanoyl chloride was observed after only a few hours of reaction time. Although this rather crude experiment should not be overinterpreted, it served as justification to go through the expense of single crystal experiments.

More precise insight was obtained by testing the reaction with properly cut single crystal surfaces. In order to compare the reactivities of surface atoms of different coordination number the activities of low energy (111), stepped (110) and (755), and stepped and kinked (976) single crystal Pd were investigated (see Scheme II and Table IV). The single crystals, as obtained from the polishing procedure, were used as catalysts with heptanoyl chloride in cyclopentane as solvent in the presence of hydrogen. Special care was taken to predry the hydrogen, solvent, and glassware. The reactions were conducted at room temperature under normal pressure without any agitation of the reaction

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(19) Koel, B. E.; Crowell, J. E.; Mate, C. M.; Somorjai, G. A. *J. Chem. Phys.* **1984**, *88*, 1988 and ref 1–20 cited therein.

(20) For a general introduction into surface science related to catalysis see: Somorjai, G. A. "Chemistry in Two Dimensions"; Cornell University Press: New York, 1984.

**Table IV.** Acid Chloride Reduction on Single Crystal Surfaces

| Pd single crystal | % aldehyde after the following time (h) of reaction | | | | turnover freq[a] (after 1 h), mol/(site s) |
|---|---|---|---|---|---|
| | 1 | 6 | 16 | 52 | |
| 111 | no conversion detectable after 3 days | | | | |
| 110 | no reaction | | | | |
| 755 | 0.8 | 1.0 | 1.2 | 2.2 | 1.2 |
| | 0.3 | 0.6 | 0.9 | 1.3 | |
| 976 | 2.3 | 4.7 | 6.0 | 6.0 | 6.0 |
| | 1.6 | 3.2 | | | |

[a] For the calculation of the turnover frequency we used $0.2 \times 10^{15}$ and $0.12 \times 10^{15}$ as concentrations for the active sites/cm$^2$ for the 755 and the 976 surfaces, respectively.

mixture. The experiments were reproducible, and the results are summarized in Table IV.

The absence of any reaction on the low energy (111) surface not only confirms the Pd-foil results but also eliminates the uncovered crystal edges as carriers of active sites. The same (111) single crystal surface was found to be active and selective in our parallel studies on the cis-selective semihydrogenation of alkynes (even after exposure to acid chlorides).[21] Since catalytic activity for hydrogenation was maintained for days on this surface carbonation or irreversible adsorption of organic compound can be excluded as being responsible for the lack of activity in the case of acid chloride hydrogenolysis. From the aldehyde formation obtained with the (755) crystal surface we conclude that step atoms are prerequisites for catalytic activity for acid chloride hydrogenolysis. However, the step distance appears to be a factor for the catalytic activity since the most highly stepped surface, the (110), was found to be inactive. At this point we cannot draw precise conclusions about the origin of the difference in activity of the two stepped surfaces. However, considering the size of an alkanoyl chloride group and the dimensions on a Pd surface it is likely that the lack of any terrace on the (110) surface is responsible for the lack in activity and the presence of small terraces, such as on a {112}, {013}, or a {123} surface, should result in the same activity as the 755) surface studied.

It is important to point out that these experiments were conducted on an overall surface area of about 4 cm$^2$ which is smaller by a factor of $10^{-4}$ than a regular supported Pd catalyst. The large turnover frequencies observed initially on these single crystals are taken as strong evidence that the dominant surface structures on the crystal faces used represent or are direct precursors of the active sites. The rapid loss of activity observed in these single crystal experiments was attributed to carbonation of the limited number of active sites available. This was confirmed by the fact that activity could be restored readily by oxidation of the single crystal with $O_2$ in the gas phase. The X-ray Laue pattern of these used and reactivated single crystals proved that the bulk lattice structure had been preserved under our mild experimental conditions. In preliminary experiments we had destroyed a (111) Pd single crystal by simple reduction in $H_2$ at 120 °C which had resulted in a destruction of the lattice structure due to an expansion of the crystal (probably formation of $\beta$-hydride[12]). However, at room temperature we have not experienced such drastic changes with single crystals. To make sure that under the mild reaction conditions studied no major surface rearrangement had occurred with the Pd crystals the (755) crystal was repolished. The Laue pattern showed proper crystal orientation. The second experiment with this surface, see Table IV, was performed with the repolished crystal.

The purpose of these experiments was to detect the catalytic activity of the dominant single crystal surfaces under "contaminated" conditions. Although this does not prove that step atoms represent the active site, it proves that they have to be present to observe catalytic activity. The proper crystal orientation and the cutting angle used in the preparation of the single crystals are taken as sufficient evidence for the dominant surface structure for the above experiments. The missing link between the single crystal experiments and the investigations with the Pd/C catalysts discussed above is the location and identification of stepped surfaces on the rearranged Pd/C catalysts. This task was attempted by transmission electron microscopy and diffraction.

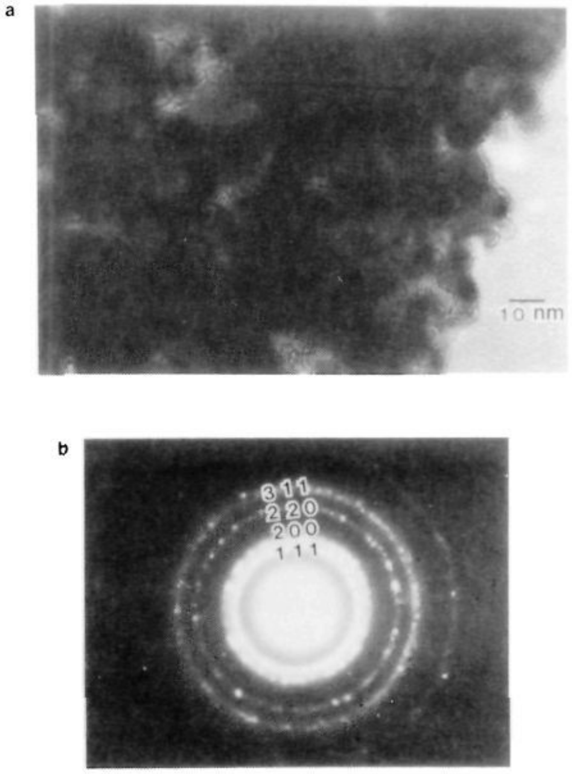

**Figure 2.** (a) Electron micrograph of fresh Pd/C catalyst showing large areas of the carbon support film covered by Pd particles. (b) Corresponding selected area electron diffraction pattern. The diffraction pattern corresponds to fcc crystalline Pd in random distribution.

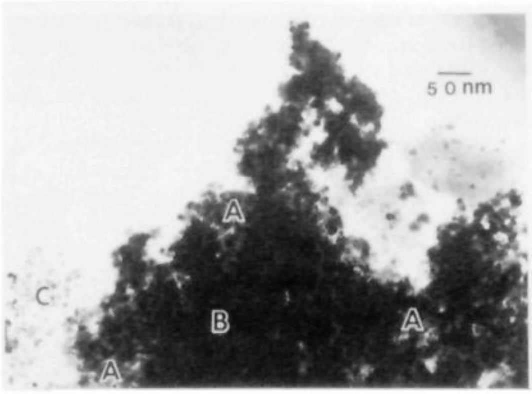

**Figure 3.** Electron micrograph of Pd/C catalyst pretreated in xylene. Three types of regions, A, B, and C, are marked.

**6. Transmission Electron Microscopic Studies.** A variety of Pd catalysts on different supports have been investigated by transmission electron microscopy recently,[22] and Plummer et al.[23] have noted the formation of thin, essentially two dimensional Pd particles upon calcination of a Pd/alumina catalyst. In the present work Pd particles on carbon supports resulting from various catalyst pretreatments such as the fresh 10% Pd/C, the Pd/C that

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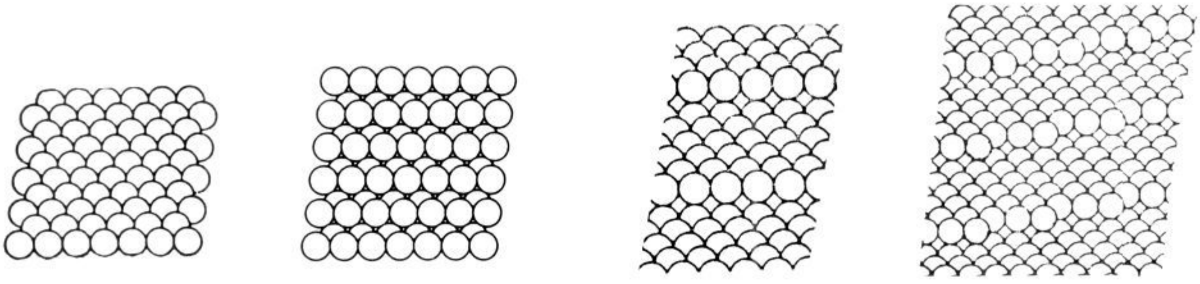
(21) Ulan, J. G.; Maier, W. F., unpublished results.

(22) Szymura, J. A. *Rev. Roum. Chim.* **1983**, *28*, 597. Chen, J. J.; Ruckenstein, E. *J. Catal.* **1981**, *69*, 254. Millward, G. R. *J. Catal.* **1980**, *64*, 381. White, D.; Baird, T.; Fryer, J. R.; Freeman, L. A.; Smith, D. J. *Ibid.* **1983**, *81*, 119. Bartholomen, L. H.; Pannell, R. S.; Fowler, R. W. *Ibid.* **1983**, *79*, 34. Schmidt, L. D.; Wang, T.; Vasquez, A. *Ultramicroscopy* **1982**, *8*, 175.

(23) Plummer, H. K., Jr.; Shinozaki, S.; Adams, K. M.; Gandhi, H. S. *J. Mol. Catal.* **1983**, *20*, 251.

**Scheme II.** Schematic Representations of Surface Structures of Single Crystal Used



[111] low energy terrace

[110] stepped

[755] stepped

[976] stepped and kinked

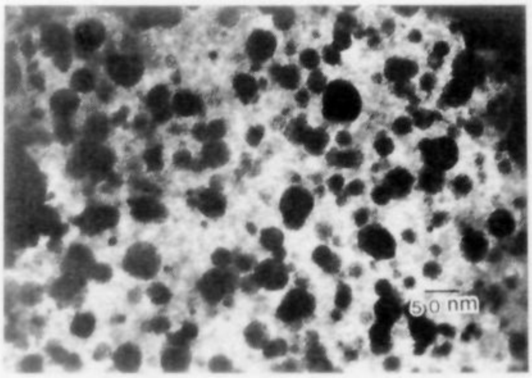


**Figure 4.** Electron micrograph of Pd/C catalyst annealed at 1000 °C. In this case Pd particles are of nearly spherical shape.

had been refluxed in xylene with and without quinoline and sulfur in the presence of hydrogen, and the catalyst that had been annealed at 1000 °C with hydrogen for 12 h (see Table II and Figure 1) have been examined. The micrographs presented in Figures 2–4 were especially selected from the many pictures taken from multiple samples to represent the gross appearance of the catalysts.

Figure 2a,b shows the electron micrograph of the fresh Pd/C catalyst along with its corresponding selected area electron diffraction pattern. It is quite evident that the carbon surface of the fresh catalyst is homogeneously covered by small Pd particles of sizes 4–10 nm (Figure 2a). The selected area electron diffraction shows a ring pattern corresponding to the crystalline fcc Pd in random distribution. The catalysts pretreated by reflux in xylene alone and in xylene in the presence of quinoline and sulfur show the same particle morphology when examined by transmission electron microscopy. Figure 3 shows an electron micrograph of the catalyst rearranged in xylene. The corresponding selected area electron diffraction pattern shows a ring pattern corresponding to the crystalline fcc Pd particles in random distribution. By careful inspection of Figure 3, three types of regions can be identified: (A) thin Pd particles on the carbon support, (B) concentrated agglomerations of Pd particles, and (C) isolated Pd particles on otherwise uncovered carbon.

Subsequent reinspection of the fresh catalyst confirmed that none of these regions could be detected on the untreated catalyst. This points to considerable surface migration and rearrangement of the Pd particles at a relatively low temperature (140 °C) which demonstrates an unprecedented lack of metal support interaction. The average particle size of 20 nm is larger compared to that in fresh catalysts, which is in agreement with the reduced metal surface area (see Table I). The micrographs obtained from the catalyst refluxed in xylene in the presence of quinoline and sulfur showed the same gross structure as the xylene refluxed catalyst shown in Figure 3.

Figure 4 shows a representative electron micrograph of the Pd/C catalyst that had been annealed at 1000 °C with hydrogen for 12 h. It was found (Figure 4a) that the Pd particles are of nearly spherical shape and of wider range of sizes but comparatively larger than the other two cases discussed earlier (average size = 100 nm). The corresponding selected area electron diffraction shows the ring pattern corresponding to the crystalline fcc Pd particles in random distribution.

For further characterization, all three catalysts were examined at higher magnification employing lattice imaging technique whose role in revealing direct information about the state of aggregation of supported metal catalysts has already been established.[20] As stated earlier in the case of fresh catalysts, most of the carbon support was found to be covered with Pd particles and the high resolution micrographs show the granular structure (characteristic feature of amorphous carbon) in the carbon region and black contrast in the Pd particles (see Figure 5a).

In the xylene refluxed Pd catalyst three types of regions, termed A,B,C were found. On region A some of the Pd particles were found suitable for high resolution electron microscopy and in fig. 5 (b,c,d) are representative examples of three different areas of type A region. It may be noted from fig. 5b,c that the spacings (~0.22 nm) of one dimensional lattice fringes corresponds to the periodicity of {111} planes of Pd. However, from only one dimensional lattice fringes, the orientation of the particle cannot be determined. Fig. 5d is a high resolution image where two dimensional lattice fringes are visible in one particle. In this case the particle orientation is $\langle 011\rangle$ and the spacing of the fringes (~0.22 nm) correspond to the periodicity of two sets of {111} planes of Pd. Careful inspection of Fig. 5d also shows that the particle is twinned (marked by arrow). Regions B and C are not found suitable for high resolution electron microscopy.

In the Pd/C catalyst annealed at 1000 °C, at many places coagulation of Pd particles occurred or else individual particles assumed spherical morphology so they were far too thick to allow lattice imaging. An example from Pd/C catalyst annealed at 1000 °C is shown in Figure 5e.

As can be seen from Table III, the fresh catalyst is too active, resulting in overreduction of the aldehydes produced; the xylene refluxed catalyst shows the desired catalytic selectivity; the catalyst heated to a 1000 °C has lost all catalytic activity (see Table II and III). The single crystal results point to steps as the active and selective sites on Pd surfaces for aldehyde formation from alkanoyl chlorides. In order to allow any correlation of the single crystal results with the Pd reconstructions on the supported catalysts (xylene refluxed) the identification of the exact orientation of the individual Pd particles in the Pd/C catalyst is desirable. For this the microdiffraction technique has been employed to characterize the orientations of Pd particles in all three cases. From the microdiffraction studies, it was found that Pd particles are in random orientations in each case. The main orientations identified from microdiffraction studies are $\langle 011\rangle$, $\langle 001\rangle$, $\langle\bar{1}12\rangle$, $\langle 013\rangle$, $\langle\bar{2}33\rangle$, $\langle\bar{1}23\rangle$, $\langle\bar{1}14\rangle$, $\langle\bar{1}22\rangle$, and $\langle\bar{1}11\rangle$. Figure 6a–c shows the microdiffraction pattern in $\langle 011\rangle$, $\langle 013\rangle$, and $\langle\bar{1}12\rangle$ orientations. A statistic of these different orientations in each case is given in Table V.

Thus from the selected area electron diffraction, lattice imaging, and microdiffraction studies the Pd particles in all three catalysts

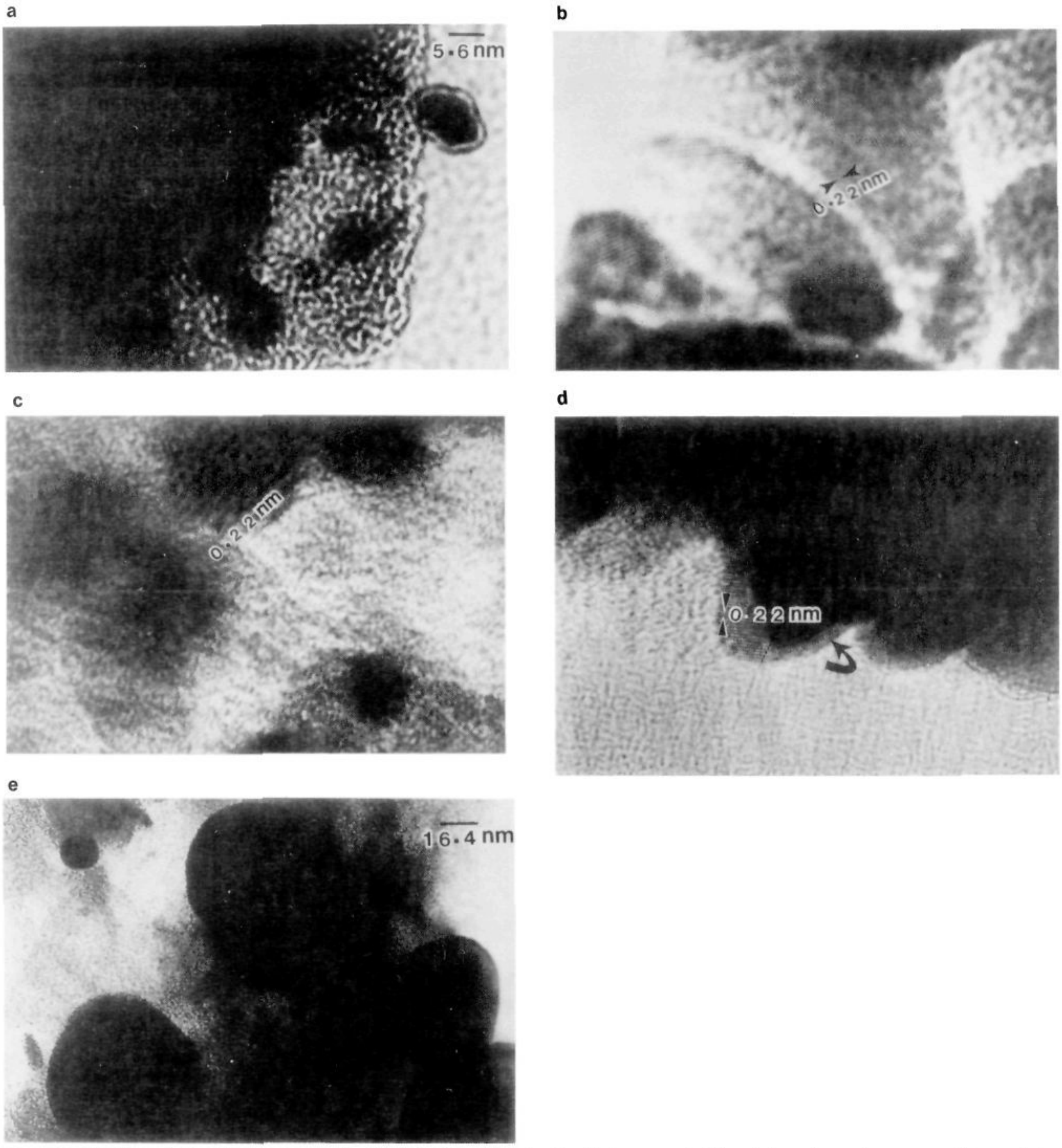


**Figure 5.** (a) High resolution electron micrograph of fresh Pd/C catalyst, showing black contrast in Pd particles and granular structure (characteristic feature of amorphous carbon) of carbon support. (b) High resolution electron micrograph of the Pd/C catalyst pretreated in xylene from a region such as A in Figure 3. One-dimensional lattice fringes corresponding to the periodicity of {111} planes ($d$ = 0.22 nm) are visible in the small crystalline Pd particles. (c) High resolution electron micrograph from another region such as A of Figure 3 showing one-dimensional lattice fringes in Pd particles corresponding to the periodicity of {111} planes ($d$ = 0.22 nm). (d) High resolution image from yet another region A (Figure 3) showing two-dimensional lattice fringes ($d$ = 0.22 nm) in one Pd particle as well as microtwinning (marked by arrow). In this case the particle is lying in the $\langle 011\rangle$ orientation. (e) High resolution image of the Pd/C catalyst annealed at 1000 °C. Black contrast in the Pd particle (nearly spherical in shape) and granular structure of carbon support is visible.

**Table V.** Statistics of the Different Orientations of the Three Catalysts by Microdiffraction Analysis

| | different orientations in % | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| catalysts | $\langle 011\rangle$ | $\langle 013\rangle$ | $\langle \bar{1}12\rangle$ | $\langle \bar{1}14\rangle$ | $\langle \bar{1}23\rangle$ | $\langle \bar{1}22\rangle$ | $\langle 001\rangle$ | $\langle \bar{1}11\rangle$ | $\langle \bar{2}33\rangle$ |
| Pd/C fresh | 12 | 6 | 8 | 4 | 4 | | 5 | | 4 |
| Pd/C xylene treated | 16 | 15 | 6 | 8 | 4 | 2 | 2 | 4 | 2 |
| Pd/C annealed at 1000 °C | 15 | 12 | 5 | 5 | 3 | 3 | 3 | 5 | |

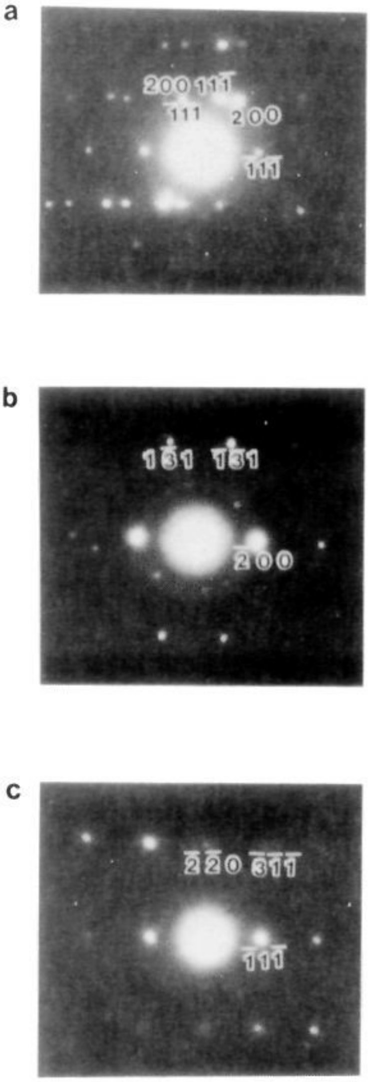


**Figure 6.** (a) Microdiffraction pattern from a twinned Pd particle (from fresh Pd/C catalyst) in the ⟨011⟩ orientation. (b) Microdiffraction pattern from a single Pd particle (from the xylene pretreated Pd/C) in the ⟨013⟩ orientation. (c) Microdiffraction pattern from a single Pd particle (from Pd/C annealed at 1000 °C) in the ⟨112⟩ orientation.

are found to be in random orientations and hence have a range of surface structures and step densities. It is difficult therefore to obtain direct one-to-one correspondence between the reactivity and overall particle structures apart from the single crystal experiments.

## Conclusion

These studies have revealed that the Rosenmund reaction is a complex reaction sensitive to a variety of parameters. Pd/C as a liquid-phase catalyst in the presence of hydrogen constantly changes its surface structure and thus catalytic activity during the reaction. During the morphological changes a buildup of larger globular Pd particles as well as the thin single crystal Pd particles (plates) were observed. From single crystal experiments stepped surfaces were identified as being essential for catalytic activity in this hydrogenolysis reaction. The most significant difference detected among the catalysts is the formation of thin Pd particles which are only present on the selective catalysts. The lack of activity observed with the annealed catalyst excludes large spherical particles as an important carrier of active sites. This suggests that the size and shape of the particles observed by transmission electron microscopic studies (Figures 2–4) may be correlated with the selectivity of this reaction. However, from transmission electron microscopic studies (Table V) it was not possible to obtain a one-to-one correspondence with reactivity and particle orientation due to randomness of the latter. Thus the active surfaces on the Pd/C catalysts have a range of orientations and hence a range of surface structures and step densities.

Promotion of the rearrangement processes of the catalyst metal and successful surface competition with the aldehyde formed appear to be the major action of the modifiers and poisons used in the reaction. Selectivity in the reaction can be achieved by the catalyst itself once brought into the desired morphological stage (metastable state) but also by the successful surface competition of added modifiers and the HCl formed. The success of many Rosenmund reactions reported is probably based on a combination of both.

The continuing reconstruction process of the Pd under reaction conditions most probably causes all the problems encountered with reliability and reproducibility of such Pd catalysts. Kinetic data obtained with such a catalyst are meainingless as long as these morphological reconstruction processes cannot be controlled. The experimental skill associated with this reaction appears to be the tailoring of the individual reaction conditions, so that the reactive fresh catalyst is deactivated fast enough not to cause considerable overreduction (Pd surface rearrangement) and to maintain conditions where the catalyst is not deactivated by the proceeding rearrangement before the reaction is completed. Since any individual substrate will not only affect the reaction rate of hydrogenolysis but also the rate of catalyst rearrangement, it is impossible to recommend a reliable general procedure for this reaction. However, the insight achieved should be helpful to the experimental chemist to guide tailoring of the reaction conditions to individual substrates.

Although our results are more qualitative we have demonstrated that the Rosenmund reaction itself is a rather simple one. We have also shown that new insight into catalytic reactions is obtained by the combination of methods developed in the fields of surface science, material science, classical heterogeneous catalysis, and organic chemistry. The complexity of the reaction is introduced by the unprecedented ability of the dispersed Pd particles on the fresh catalyst to undergo drastic morphological changes under the influence of substrates and organic solvents in a hydrogen atmosphere which amplify previous reports on the change of bulk and surface structure of palladium catalysts during reactions.[24] These uncontrolled changes in the morphology of the catalyst make a quantitative description of the reaction too complicated.

## Experimental Section

For GC analysis a SP-1200 column (6 ft × 0.25 in.) from Supelco was used on a Varian 920 GC. The column was chlorinated once a day prior to the analysis by injection of 100 $\mu$L of oxalyl chloride. The hydrogen was purified by a deoxygenizer cartridge and 3 Å molecular sieve. All solvents were distilled from $LiAlH_4$. Acid chlorides were freshly prepared every week with oxalyl chloride by standard procedures, purified by distillation, and stored over 3 Å molecular sieve under nitrogen. As catalysts were used 10% Pd/C (Aldrich) and 5% $Pd/BaSO_4$ prepared according to a procedure by Mosettig.[2] Xylene was freshly distilled from calcium hydride, the HPLC grade cyclopentane was used as received, and *n*-octane was distilled from $LiAlH_4$.

**Rate Studies (See Figure 1).** In a 50-mL three-neck round-bottom flask equipped with condenser, $H_2$ inlet, and septum for reagent addition and sampling, 100 mg of 10% Pd/C was predried at 150 °C in a stream of $N_2$ for 24 h, 25 mL of xylene, and the modifier (see below) were added and refluxed under $H_2$ for 4 h. Under a slow stream of $H_2$ 5 mL of the xylene were distilled off. The heating was interrupted, 2 mL of acid chloride were added, and the reaction was carried out under gentle reflux and stirring. The reaction was monitored by GC; samples were taken every 15 min during the first 2 h, every 30 min during the next 6 h, and about every 12 h thereafter. The modifiers used were 20 $\mu$L of a quinoline and sulfur solution (prepared from 6 g of quinoline and 1 g of sulfur, refluxed for 5 h, diluted with xylene to 70 mL),[2] 2 mg of quinoline, and 0.4 mg of sulfur. In one experiment the xylene was replaced by *n*-octane.

**Surface Area Determination.** The surface area determinations were performed on a Perkin Elmer Adsorptometer. The Pd catalyst (500 mg) was first heated to 200 °C in a stream of argon (20 mL/min) for at least 10 h to remove any surface adsorbates and water. Then the surface was

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(24) Janko, A.; Palczewska, W.; Szymerska, I. *J. Catal.* **1980**, *61*, 264.

titrated at room temperature with oxygen. Oxygen in portions of about 0.2 mL was added to the stream of arrgon until the thermal conductivity detector responded with identical areas after two subsequent injections, indicating complete surface oxidation. This procedure was repeated with hydrogen in portions of about 0.1 mL and the amount of hydrogen adsorbed was noted. This whole oxidation/reduction procedure was now repeated at least 2 times. If the three hydrogen adsorption values were within 5% the average of the three measurements was taken to determine the surface area, otherwise the measurement was repeated until the data were consistent (in the case of the pretreated catalysts consistent adsorption was usually achieved after 5 cycles, indicating initial surface adsorbates or removable carbonation). The surface area was calculated by assuming a surface area of 7.7 Å$^2$ per Pd surface atom according the following reaction: $PdO + {}^3/_2H_2 \rightarrow PdH + H_2O$. Every time the equipment was used, its performance was tested with the fresh Pd/C catalyst first.

**Single Crystal and Foil Experiments.** A palladium single crystal was cut within 1° of the desired ⟨111⟩, ⟨110⟩, ⟨755⟩, and ⟨976⟩ orientations by standard procedures. The resulting plates (thickness ≤ 1 mm) had about a 4 cm$^2$ total surface area (both sides) of which less than 5% was polycrystalline (edges only). They were analyzed for the correct structure orientation by LAUE X-ray back scattering. After the first experiment each crystal was treated with oxygen at 400 °C for 2 h before the experiment was repeated. The reactions with single crystals were performed in a 100-mL round-bottom flask. The crystals were transferred in the reaction flask under nitrogen atmosphere and covered by cyclopentane as a solvent (10 mL). After the flask was flushed with hydrogen the reaction was started under a hydrogen atmosphere by adding 0.1 mL of acid chloride via syringe. A positive hydrogen pressure was maintained by the use of a balloon. The reactions were carried out in the absence of any stirring or agitation in order to avoid possible harm to the single crystals. The reactions were monitored by GC. The foil experiments were done under identical conditions on a commercial Pd foil (thickness 0.025 mm) with a total of about 20 cm$^2$ surface area. All single crystals had lost their mirror surface after the first experiment and some bending was visible after the treatment in $O_2$. However, despite these macroscopic changes the experimental activity and selectivity were maintained.

The Pd foil was used without any pretreatment. In one experiment the roughness was increased by the use of a very fine abrasive.

**Electron Microscopy Studies.** Specimens (Pd/C) in the form of powder 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 transmission electron microscope.

Microdiffraction analysis was done in the STEM mode from individual particles by choosing a small probe. The statistical analysis was obtained in each case from the inspection of nearly 100 particles observed on several specimen.

**Experimental Recommendations.** On the basis of the experience from this investigation no generally reliable procedure for successful Rosenmund reduction can be offered. However, a few recommendations may be helpful to overcome the usual problems. As mentioned already most important for a successful reaction is to carefully dry all reagents involved, including the catalyst (dry Pd catalyst is highly pyrophoric!). Acid chlorides should be prepared with oxalyl chloride. *n*-Octane or any other nonepolar solvent will be helpful to achieve a fast reaction rate. A 10:1 ratio of catalyst to substrate is recommended. A 1–2 h reflux of the catalyst under hydrogen in *n*-octane (or xylene) prior to the reaction will be sufficient to cause the necessary deactivation. The reaction itself is usually fast enough at room temperature. For larger scale reaction a constant flow of hydrogen is recommended to allow removal of the hydrogen chloride formed which otherwise can cause severe reduction of the reaction rate. Reactions with a new substrate should be monitored by GC (chlorinated acidic column). If alcohol formation is observed the addition of 0.1% up to equivalent amounts of an amine (any amine, known not to react with substrate and product, that can be separated readily should be helpful) should solve the problem. This addition may be done immediately upon recognition of overreduction or even before the initial deactivation. This amine addition, however, will slow down the reaction. In the case of a slow reaction the amine addition should be omitted and a larger catalyst substrate ratio together with an increased reflux time prior to the reaction should suffice. If overreduction remains a problem equivalent amounts of benzaldehyde in the reaction mixture should prevent the desired aldehyde from surface interaction. The used catalyst may often be the most selective and in the case of fast reactions may well be used for subsequent reactions.

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**Registry No. 1**, 2528-61-2; **2**, 98-88-4; Pd, 7440-05-3.