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Palladium-catalyzed hydrogenation without hydrogen: the hydrodechlorination of chlorofluorocarbons with solid state hydrogen over the palladium (111) crystal surface and its implications

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The hydrogenation of chlorofluorocarbons (CFC's, 1,1-dichlorotetrafluoroethane, $CCl_2F–CF_3$) was found to be positive 1/2 order in hydrogen pressure over palladium foil while it was zero order in hydrogen pressure over palladium single crystals regardless of their orientation ((111), (100)). When hydrogen was completely removed from the gas phase, hydrogenation continued for about 10^4 turnovers over palladium single crystals which were pre-exposed to hydrogen. Solid state hydrogen, stored in the bulk of a palladium single crystal, was found to be responsible for the hydrodechlorination of $CCl_2F–CF_3$ in the absence of gas phase hydrogen. Lower reaction rates and increased selectivity for overhydrogenation to produce $CH_3–CF_3$ indicate that the nature of hydrogenation with solid state hydrogen in palladium is different from hydrogenation with gas phase hydrogen. The use of solid state hydrogen for various chemical processes instead of gas phase hydrogen has advantages that are enumerated.

Keywords: hydrodechlorination, solid state hydrogen, Pd(111), 1,1-dichlorotetrafluoroethane, CFC 114a

For environmental reasons chlorofluorocarbons (CFC's) are increasingly replaced by "ozone friendly" (non-chlorinated) hydrofluorocarbons (HFC's) as refrigerants, propellants, etc. [1–3]. The hydrodechlorination of 1,1-dichlorotetrafluoroethane to 1,1,1,2-tetrafluoroethane ($CCl_2F–CF_3 + 2H_2 \rightarrow CH_2F–CF_3 + 2HCl$) is an important palladium-catalyzed reaction that converts an environmentally harmful molecule to another that has no destructive effect on stratospheric ozone. During our studies of the kinetics and the mechanism of this reaction using palladium foil and (111) and (100) single crystals as model catalysts we detected a dramatic change in the hydrogen pressure dependence of the reaction rate when we exchanged the palladium foil for the single crystals. While the reaction rate varied with positive 1/2 order in hydrogen pressure over the palladium foil [4], it became independent of hydrogen pressure (i.e. zero order) over the single crystals regardless of their crystallographic orientations ((111), (100)) that were used [5]. Figure 1 shows the hydrogen pressure dependence of the reaction rate for the different surfaces under typical reaction conditions of $p(CCl_2F–CF_3)$ of 75 Torr (1 Torr=133 Pa) and at a temperature of 423 K. Reaction rates are presented in the form of turnover frequencies, i.e. molecules produced per Pd surface atom per second. For every experiment the Pd catalysts were cleaned in ultrahigh vacuum (uhv) by argon sputtering and characterized by Auger electron spectroscopy (AES) and low energy electron diffraction (LEED), before they were transferred into the reaction cell under uhv [6,7]. The model catalysts were then exposed to the reactant mixture of $CCl_2–CF_3$ and H_2 at 373 K (the elevated temperature is necessary to avoid the formation of β Pd hydride which would lead to embrittlement of the crystal [8–10]) and subsequently heated to the reaction temperature of 423 K (heating rate 1 K s^{-1}).

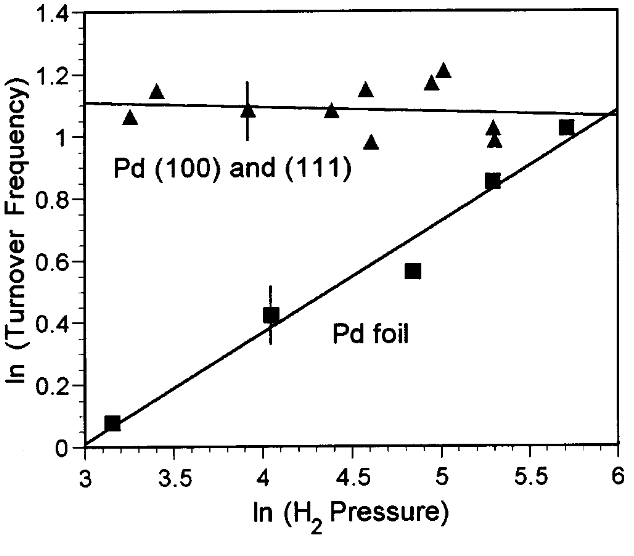

Figure 1. Determination of the hydrogen reaction order for palladium single crystals and foil in the hydrodechlorination of $CCl_2F–CF_3$. Experiments were run at 423 K, 75 Torr $CCl_2F–CF_3$, 20 to 200 Torr H_2. The turnover numbers were corrected for an HCl pressure of 0.1 Torr.

In order to explore the reason for the surprising difference in the hydrogen pressure dependence we gradually reduced the hydrogen pressure over the palladium (111) single crystal down to 5 Torr. We expected to observe 1/2 order at very low H_2 pressures originating from different pressure regimes on the foil and on the single crystals. However, the reaction rate still remained independent of hydrogen pressure indicating a saturation in H_2.

This result suggests that the hydrogen stored in the bulk of the palladium crystal plays an important role in the course of the reaction. Finally *all* of the hydrogen was removed from the gas phase in the reaction cell but the Pd crystal was pre-exposed to hydrogen at 373 K for 30 min. The hydrogen atmosphere was removed before the CFC was introduced and the reaction started. In spite of the *absence* of gas phase hydrogen the hydrogenation (hydrodechlorination) reaction could be sustained for about 10^4 turnovers before it stopped. It appeared that the hydrogen stored in the bulk of the palladium single crystal continued the hydrogenation of $CCl_2F–CF_3$ under the reaction conditions employed.

This is shown in figure 2 in an accumulation versus time plot for reactions with gas phase and "solid state" hydrogen. The number of product molecules is normalized per surface Pd atom and is given as turnover number (TON). Only TON's for the main product $CH_2CHF–CF_3$ are included in figure 2 but the rates of formation of under-hydrogenated and over-hydrogenated compounds ($CFClH–CF_3$, 1-chloro-1,2,2,2-tetrafluoroethane and $CH_3–CF_3$, 1,1,1-trifluoroethane) are given in table 1. The curvature in the TON vs. time plots is due to the inhibition by HCl, in which the reaction order is −1. The inhibition by HCl causes the turnover rate to depend strongly on the degree of conversion, therefore all rates presented are corrected for an HCl pressure of 0.1 Torr (i.e. for nearly identical conversions) [4].

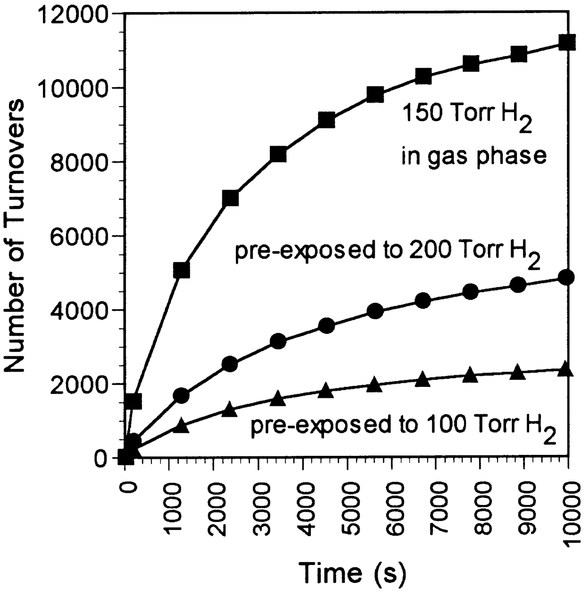

Figure 2. Accumulation vs. time plot for the hydrodechlorination of $CCl_2F–CF_3$ (75 Torr) on Pd(111) with gas phase and solid state hydrogen at 423 K.

Since the volume of the single crystal is about 20 times greater than that of the Pd foil the amount of solid state hydrogen was also greater in proportion. As a result the contribution of solid state hydrogen, with solubility in the 1 H/10^3 Pd atom range (far below the concentration needed to form β Pd hydride), to the hydrogenation became significant for the crystals while it was negligible for the small volume Pd foil compared to hydrogenation by H_2 in the gas phase. In order to prove hydrogenation by the solid state hydrogen in palladium conclusively and to rule out any sources of hydrogen other than the Pd crystal itself, the following "blank" studies were performed.

In the first control experiment H_2 was recirculated in the reaction cell while the cleaned and annealed Pd crystal was still kept in the UHV chamber. The reactor was then cleaned by repeated sequences of purging with Ar and evacuation before the annealed Pd crystal was transferred into the reaction cell. After $CCl_2F–CF_3$ was subsequently added, *no* hydrodechlorination reaction was observed thereby proving that no hydrogen is trapped in the reaction cell or in the gas lines.

In the second set of control experiments an annealed Pd(111) crystal was transferred to the reaction cell and exposed to 200 Torr H_2 at 373 K for 40 min. The hydrogen was then pumped off, and the crystal cooled to about 303 K before it was moved back to the uhv chamber (during sample transfer no heating is possible), where it was kept at room temperature. The reaction cell was cleaned by repeated purging with Ar and evacuation before the hydrogen pre-exposed crystal was transferred back into the reaction cell. After adding 75 Torr $CCl_2F–CF_3$ the formation of $CH_2F–CF_3$ was observed and the rate was identical to the solid state reaction presented in figure 2. Under these conditions the initial turnover frequency is about eight times smaller than in the corresponding gas phase reaction (table 1).

The palladium crystals could be filled with hydrogen at 100 and at 200 Torr and at 373 K within 15 to 60 min. After the hydrogen was pumped off, the temperature was decreased to 343 K to reduce the loss of H_2 during cleaning the reaction cell. As expected the hydrogenation turnover rate as well as the conversion of $CCl_2F–CF_3$ to $CH_2F–CF_3$ were higher when 200 Torr of hydrogen was used (0.5 vs. 0.2% after 2.5 h).

We found that the rates of hydrogen diffusion into or out of the Pd crystals were negligibly slow at 298 K. We had to heat the Pd catalyst to at least 373 K to detect the hydrodechlorination reaction. As a consequence the solid state hydrogen could be removed by heating the crystal at 373 K or above in vacuum. Conversely, the stored solid state hydrogen filled Pd crystal could be transferred or otherwise manipulated at 298 K without significant loss of bulk hydrogen. Thermal desorption

Table 1
Palladium-catalyzed hydrogenation (hydrodechlorination) of chlorofluorocarbons on Pd(111) with solid state and gas phase hydrogen [a]

	Turnover frequency (s^{-1}) (Selectivity (%))			H/Pd
	$CH_2F–CF_3$	$CFClH–CF_3$	$CH_3–CF_3$	
reaction with H_2 in the gas phase (150 Torr)	12.30 (82)	1.53 (10)	1.26 (8)	–
reaction with H_2 in solid state (pre-exposed to 200 Torr H_2)	1.60 (80)	0.08 (4)	0.33 (16)	3.5×10^{-3}
reaction with H_2 in solid state (pre-exposed to 100 Torr H_2)	0.42 (78)	0.03 (5)	0.09 (17)	1.6×10^{-3}

[a] $CCl_2F–CF_3 = 75$ Torr, $T = 423$ K, corrected for 0.1 Torr HCl.

studies on Pd single crystals [11] and on Pd foil [12] have shown that bulk hydrogen is desorbed in a broad peak starting around 473 K and with a maximum at $T \geqslant 600$ K.

Another interesting observation is the change in product selectivity as the hydrogen was switched from gas phase to solid state (table 1). In addition to the dominant product $CH_2F–CF_3$, small concentrations of $CFClH–CF_3$ were produced as a result of underhydrogenation and small concentrations of $CH_3–CF_3$ formed as a result of overhydrogenation. In the presence of only solid state hydrogen the concentration of the overhydrogenated product $CH_3–CF_3$ doubled. It appears that the hydrogen atoms dissolved in the Pd crystal are stronger hydrogenating agents than the hydrogen atoms produced by the dissociation of the gas phase molecules at the metal surface. The role of bulk hydrogen atoms as reactants in the hydrogenation of ethylene to ethane on Ni(111) has been recently studied by Ceyer et al. [13] using thermal desorption and high-resolution electron energy loss spectroscopy. While bulk hydrogen was active in the hydrogenation of an adsorbed sub-monolayer of ethylene at 180 K under uhv, no hydrogenation was observed for surface-bound H under these conditions. These authors formed an equivalent of ten monolayers of H absorbed in the bulk metal by exposing the Ni(111) crystal to a beam of atomic hydrogen at 130 K [14]. The concentration of bulk hydrogen was about 10^3 times smaller than in our experiments.

Our studies indicate that hydrogen atoms stored in bulk palladium can be readily available to carry out surface hydrogenation processes at 373 K or above. Solid state hydrogen could be utilized in steady state by using a hydrogen-filled, heated palladium tube where hydrogenation of reactants would be carried out outside the tube by the H atoms diffusing through bulk palladium. Potential future commercial applications of so-called "catalytic membrane reactors" have been discussed recently and the attractive features of such devices have been pointed out [15]. The possibility of obtaining different selectivities and rates with solid state hydrogen atoms as compared to the hydrogenation with surface H atoms formed by the dissociation of H_2 gas molecules is indicated by our hydrodechlorination studies. The observation that the rates of hydrodechlorination using solid state hydrogen are considerably slower than using H_2 gas is not surprising considering the approximately 1 in 10^3 solubility of hydrogen in the metal (10^{19} H in 10^{22} Pd in our crystals). It should be noted that our conditions of producing solid state hydrogen have not been optimized but the hydrogen solubilities calculated from the measured turnover numbers are comparable to those reported by Goodman and co-workers in a high-pressure kinetic study of hydrogen absorption by Pd(110) [16]. There are considerable benefits in using solid state hydrogen for certain reactions, however. When hydrogen must be used in the presence of oxygen or other oxidizers the use of solid state hydrogen can move the reaction out of the explosive range. Dilute hydrogen gas streams may be converted to more concentrated sources of reactive H atoms by using them to produce solid state hydrogen. Shifting equilibrium in reactions where hydrogen is produced may be achieved by the removal of hydrogen into bulk palladium.

Heterogeneous catalysis is usually performed by nanoparticles, in the range of 2–200 nm in diameter to optimize the surface area, since the chemical process is usually surface reaction rate controlled. If solid state hydrogen is to be utilized to carry out catalytic reactions the catalyst geometry has to be drastically modified.

Methods

Materials

The Pd(111) single crystal, a circle-shaped disc (1 mm thick, 10 mm in diameter), was cut from 5N bulk material (Goodfellow, UK) and polished by standard mechanical methods until Laue X-ray backscattering experiments showed a plane surface oriented to within 0.5° of the ⟨111⟩ direction. The Pd polycrystalline foil (Johnson Matthey, 99.99%) was 0.1 mm thick. The chlorofluorocarbon was obtained from DuPont Co. and had a purity of 99.99% with only one impurity detected, possibly $CH_2Cl–CF_3$. This impurity did not change its concentration during the experiments. The other gases used were H_2 (Matheson, prepurified) and Ar (Liquid Carbonic, 99.995%).

Apparatus

The experiments were carried out in a system which combines an ultrahigh vacuum (uhv) chamber (base pressure 7.5×10^{-10} Torr) and an uhv-compatible high pressure batch reactor (ca. 1 atm) [6,7]. Small surface area (ca. 1 cm^2) model catalysts can be transferred between the two parts (using a welded bellows assembly) while maintaning an uhv environment during sample transfer. This system allows to correlate surface characterization in uhv with kinetic measurements performed under technically relevant conditions.

The Pd surfaces were cleaned in uhv before every reaction by Ar sputtering (beam energy 1700 V, 4.0×10^{-5} Torr Ar) at 973 K for 1 h, and subsequently annealed at 973 K for 20 min. The cleanliness of the surface was controlled by Auger electron spectroscopy (AES) and low energy electron diffraction (LEED) was used to confirm the 1 × 1 structure. The Pd specimens were attached to a sample cart containing two pins for resistive heating and two pins (chromel and alumel) for thermocouple temperature readings (type K thermocouple spotwelded to the rear center of the crystal). With the help of a magnetically coupled transfer arm the sample cart with the Pd catalysts could be transferred between the surface characterization chamber and the high pressure reactor. Identical sockets for the sample cart pins were provided in the uhv chamber and in the reaction cell in order to allow heating and temperature measurement on both stations.

After the sample was transferred into the reaction cell an Ar pressure which would finally lead to a total gas balance of 1 atm was introduced first. With a recirculation pump turned on (metal bellows pump, Parker model MB 21, flow rate of about 1 $\ell\,min^{-1}$), the Pd sample was then heated to 373 K before H_2 was added. The elevated temperature prevents the formation of a bulk palladium β hydride during H_2 dosage (in an earlier experiment a Pd foil shattered after exposure to 500 Torr H_2 at room temperature because of the volume change upon formation of the hydride phase). After the reactant $CH_2F–CF_3$ was introduced the crystal temperature was rapidly increased to the reaction temperature of 423 K (at 373 K the reaction rate is about two orders of magnitude smaller). For experiments with "solid state hydrogen" the H_2/Ar atmosphere was removed before the CFC was added (using an adsorption pump and a turbomolecular pump).

The reaction products were analyzed with a gas chromatograph (Hewlett-Packard 5790A) with a flame ionization detector. The products were separated in a 5% Krytox 143AC, 60/80 Carbopack B HT 20 × 1/8″ column (Supelco).

Blank experiments were run to certify that the background catalytic activity was not significant. Those experiments were run on a stainless steel foil and at 423 K background reactions could not be detected.

After each reaction, Ar sputtering for 1 h at 973 K followed by annealing was sufficient, as shown by AES, to clean the surface.

Data analysis

The curvature in the TON vs. time plots is due to the inhibition by the reaction product HCl, in which the reaction order is −1. The inhibition by HCl causes the turnover rate to depend strongly on the degree of conversion. Therefore, it is necessary to integrate the rate equation. Plotting the square of concentration as a function of time results in a linearized plot whose slope is proportional to the reaction rate constant. This slope is used to calculate the turnover frequency, which can then be corrected for the desired HCl pressure [4].

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