

## Incorporation and reactivity of carbon in palladium

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**Abstract:** The incorporation of carbon into supported ( $ZrO_2$ ,  $Al_2O_3$ ,  $TiO_2$ ) and unsupported palladium has been investigated by means of thermal analysis and X-ray powder diffraction. Below  $500^\circ C$  the rate of CO disproportionation, preceding carbon incorporation, depended on the kind of support and decreased in the order:  $ZrO_2 > TiO_2 > Al_2O_3 >$  unsupported Pd. The carbon concentration in the Pd lattice declined above  $600^\circ C$  and a maximal concentration of 15 at% was only reached with supported palladium. The reactivity of the carbon in the Pd-C solid solution towards oxygen and hydrogen was significantly higher than that of the surface carbon. Partial removal of carbon from the Pd lattice already occurred during grinding at room temperature.

### INTRODUCTION

The interaction of carbon monoxide with palladium has been the subject of numerous studies due to its importance in catalytic reactions involving CO. In previous studies we have shown (1-3) that upon exposure of Pd/ $ZrO_2$  to a CO atmosphere, disproportionation of CO (Boudouard reaction) occurs with subsequent incorporation of carbon into palladium, starting at  $180^\circ C$ . This reaction has also been observed for the system Pd/ $TiO_2$  prepared by the sol-gel-aerogel route (4). In the present work, we have extended the studies on carbon incorporation to Pd supported on various oxides and unsupported pure metal. In addition, the reactivity of the interstitial carbon towards oxygen and hydrogen has been investigated.

Carbon incorporation into Pd is preceded by the Boudouard reaction  $CO_2(gas) + C(solid) = 2 CO(gas)$ . At low temperatures, the equilibrium of this reaction is shifted toward the formation of carbon and  $CO_2$ . The values of the equilibrium constant ( $K_p$ ) and Gibbs energy ( $\Delta_r G^\circ$ ) at 127, 227 and  $327^\circ C$  are:  $K_p$  - ( $5.21 \cdot 10^{-14}$ ,  $1.77 \cdot 10^{-9}$  and  $1.87 \cdot 10^{-6}$  bar) and  $\Delta_r G^\circ$  - (101.8, 83.8 and  $65.8 \text{ kJ mol}^{-1}$ ), respectively (5). At higher temperatures, the equilibrium carbon concentration decreases (at 527 and  $727^\circ C$ , the values of  $K_p$  and  $\Delta_r G^\circ$  are  $1.09 \cdot 10^{-2}$ , 1.90 bar and 30.1,  $-5.3 \text{ kJ mol}^{-1}$ , respectively (5)).

### EXPERIMENTAL AND RESULTS

Carbon incorporation into the Pd lattice was investigated using thermal analysis (TG and DTA) combined with mass spectroscopy and X-ray powder diffraction (XRD). The application of XRD was suitable due to the change of the Pd lattice constant during the formation of the solid solution Pd-C. In the face-centered cubic lattice two kinds of sites, octahedral and tetrahedral, are available for interstitial carbon incorporation. If the lattice is regarded as being built up of close-packed spheres of radius  $r$ , then the octahedral hole will contain a sphere of  $0.414r$ . The smaller, tetrahedral interstices are capable of accommodating spheres of radius  $0.225r$ . In the f.c.c. lattice, there are one octahedral and two tetrahedral holes per metal atom. Carbon is located in larger, octahedral holes only (Fig. 1), as originally proposed by Ziemecki (6) and Kaszukur (7). The ratio of C/Pd radii (0.56) indicates that the incorporation of carbon will lead to an expansion of the Pd crystal lattice, which shifts the Pd X-ray reflections to lower  $2\theta$  values. In order to quantify this relationship, samples with different amounts of incorporated carbon were prepared by varying the reaction temperature. The amount of incorporated carbon was measured by mass-spectrometric determination of the amount of evolved  $CO_2$  after reaction with oxygen. The results showing the linear relationship between carbon concentration in the lattice (at%) and the shift of the most intensive Pd(111) reflection are summarized in Fig. 2.

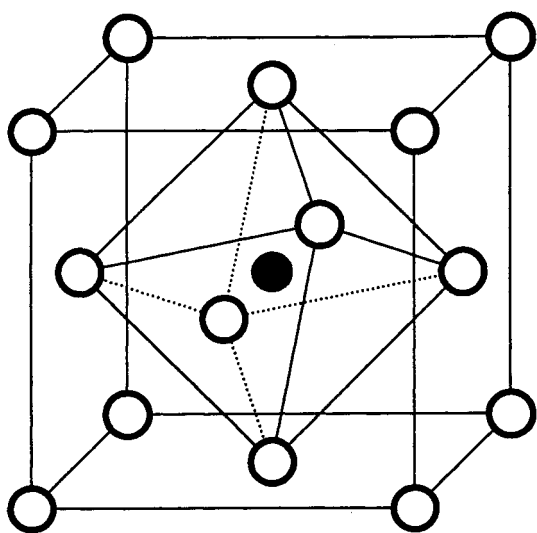


Fig. 1 Location of carbon (solid circle) in the octahedral hole of face-centered cubic Pd lattice.

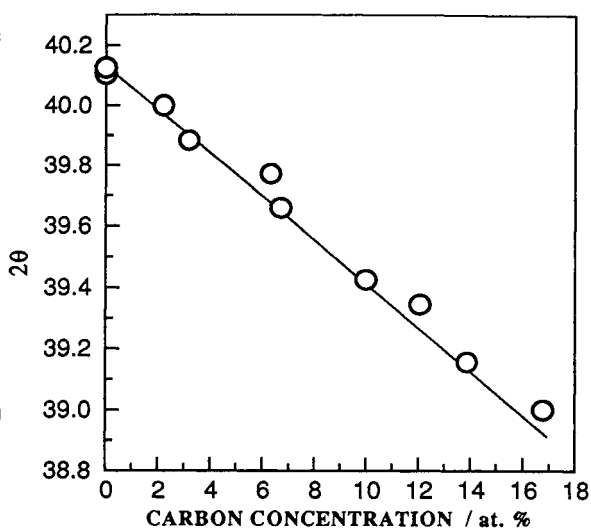


Fig. 2 Relationship between carbon concentration in Pd and position of Pd(111) reflection.

Thermoanalytical curves (TG, DTA) measured during heating of Pd (30.0 wt%)/ZrO<sub>2</sub> in pure CO (impurities < 0.005 vol%) are shown in Fig. 3. Experiments were carried out on a Netzsch STA 409 thermoanalyzer with a heating rate of 10°C min<sup>-1</sup>. The mass spectrometric curve  $m/z=44$  reveals that the disproportionation of CO over Pd/ZrO<sub>2</sub> already occurs at ca. 100°C, whereas the incorporation of carbon leading to the increase of the rate of CO disproportionation starts at ca. 180°C. The latter is indicated by the small, 0.8% weight-gain observed on the TG curve, the exothermal peak on the DTA curve centered at 230°C, and the additional peak of CO<sub>2</sub> evolution ( $m/z=44$  curve).

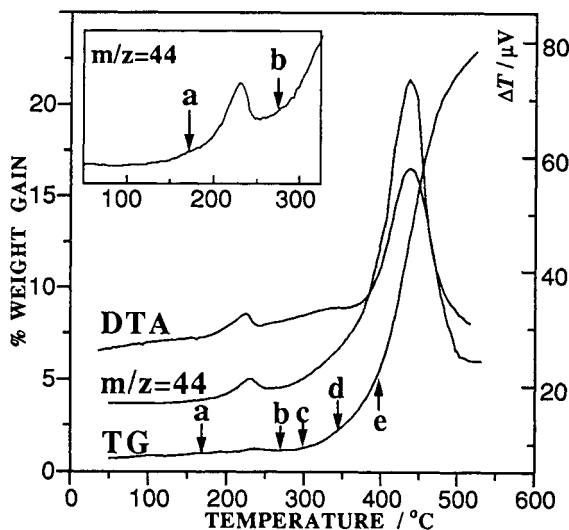


Fig. 3 Reaction of Pd/ZrO<sub>2</sub> with CO. Inset presents magnified part of  $m/z=44$  curve. Temperatures of quenching of the reaction are marked by arrows: *a*-170; *b*-275; *c*-300; *d*-350 and *e*-400°C respectively.

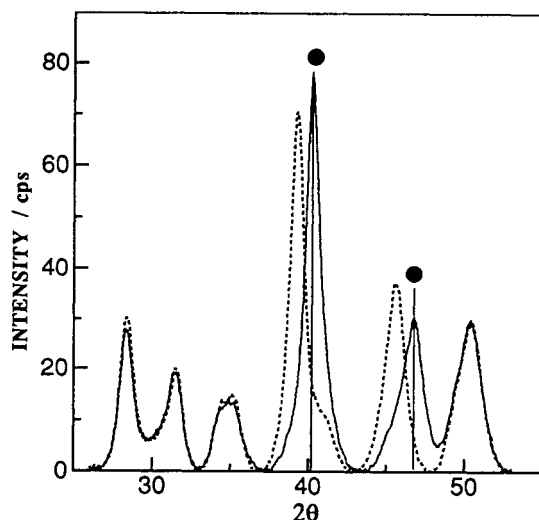


Fig. 4 XRD patterns of Pd/ZrO<sub>2</sub> heated in CO atmosphere taken before (solid line, *a*) and after (dotted line, *b*) incorporation of carbon into Pd lattice (see Fig. 3). The positions of Pd (111) and (200) reflections are marked as solid circles, other reflections are due to monoclinic ZrO<sub>2</sub>.

The gain in weight at temperatures above ca. 275°C is caused by deposition of carbon on the sample surface. Note that after the complete saturation of palladium, further incorporation of carbon produced by the Boudouard reaction above 275°C is impossible. Thus, increasing the reaction temperature above the temperature corresponding to saturation affords samples having different amounts of surface carbon (depending on the reaction temperature) and a constant amount of interstitial carbon. Such samples, which were used later for comparing the reactivity of the different kinds of carbon, were prepared by quenching the reaction (fast cooling with subsequent rapid evacuation of the system). The temperatures at which the reaction between Pd/ZrO<sub>2</sub> and CO was quenched are marked by arrows on TG curve shown in Fig. 3.

The XRD patterns of the samples taken just before and immediately after the small exothermal peak on the DTA curve and the additional peak of CO<sub>2</sub> evolution ( $m/z=44$ , see inset in Fig. 3) are presented in Fig. 4. The diffraction patterns clearly indicate the shift of the position of Pd(111) and (200) reflections due to the change of the dimensions of the palladium crystal lattice caused by carbon incorporation. This process occurs in the temperature range 180-275°C and increases the rate of CO<sub>2</sub> formation, resulting in an additional small peak on the DTA and mass spectrometric curves.

In order to check whether disproportionation of CO and carbon incorporation depend on the kind of support and the method used for the preparation of the supported Pd (impregnation, coprecipitation, preparation from amorphous alloy), the reaction was investigated over various supported palladium samples. Catalysts containing 10 wt% of Pd on ZrO<sub>2</sub>, TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> were prepared by impregnation and their reaction with CO was investigated by means of thermal analysis combined with mass spectroscopy. The corresponding results, together with the data measured for 30wt% Pd/ZrO<sub>2</sub>, prepared from an amorphous Pd-Zr alloy (1), unsupported palladium and the pure zirconia support are presented in Fig. 5. Note that CO<sub>2</sub> evolution curves ( $m/z=44$ ) are greatly different, depending on the particular catalyst preparation and the support. Unsupported palladium disproportionates CO only with low rate and incorporation of carbon begins at much higher temperatures than with supported samples, of which Pd/ZrO<sub>2</sub> is the most active. At higher temperatures, carbon dioxide concentration decreases, as expected from the temperature dependence of the equilibrium of the Boudouard reaction.

Additional information concerning carbon incorporation was obtained from XRD measurements of the samples quenched at different temperatures during their reaction with CO. XRD patterns for pure palladium are presented in Fig. 6. A distinct shift of the Pd(111) reflection to lower 2θ-values occurred, starting from ca. 320°C, i.e. when carbon began to incorporate into the Pd lattice. At higher temperatures (above 620°C), the Pd(111) reflection moved towards the position characteristic for the pure metal, indicating that carbon was being gradually removed from the lattice.

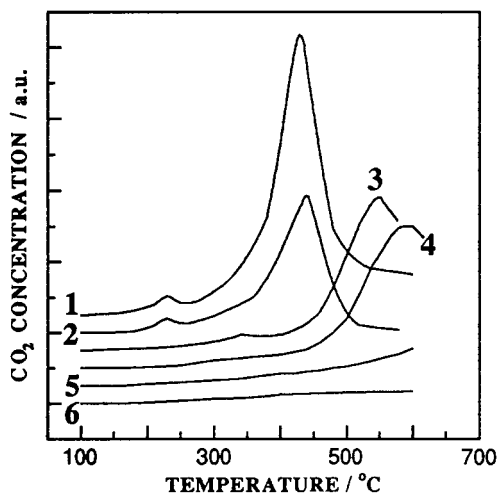


Fig. 5 Concentration of carbon dioxide formed by CO disproportionation over: 1) Pd/ZrO<sub>2</sub>- amorphous alloy, 2) Pd/ZrO<sub>2</sub>, 3) Pd/TiO<sub>2</sub>, 4) Pd/Al<sub>2</sub>O<sub>3</sub>, 5) unsupported Pd and 6) ZrO<sub>2</sub>. Samples 2-4, 10wt%Pd prepared by impregnation.

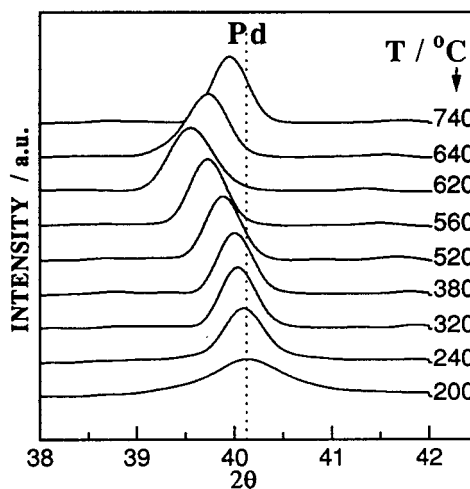


Fig. 6 Shift of the position of Pd (111) reflection as a function of reaction temperature for Pd/ZrO<sub>2</sub>.

This behaviour was observed with all samples investigated, indicating that the solid solution of carbon in palladium is only stable in a limited temperature range. The relationship presented in Fig. 2 (calibration curve) allowed the calculation of the amount of incorporated carbon as a function of the reaction temperature. The temperature ranges where saturated Pd-C exists in the samples are presented in Fig. 7.

As emerges from this figure, the kind of support distinctly influenced the temperature at which the incorporation of carbon into Pd starts. In contrast, the removal of carbon from palladium, occurring in the range 475-600°C, seems to be independent of the support, leading to the different temperature ranges for the existence of completely saturated solutions. These ranges depend on the support and decrease in the order:  $ZrO_2 > TiO_2 > Al_2O_3$ . For unsupported palladium, incorporation of carbon begins at a relatively high temperature, near that at which removal of carbon from the lattice starts to be predominant, leading to a very narrow temperature range where Pd-C phase is observed and low concentration of carbon. Maximal concentration of C in pure palladium was only ca. 6.5 at% compared to ca. 15at% determined for supported catalysts.

Data presented in Fig. 7 indicate that the Pd-C solid solution decomposes at higher temperatures, even in the presence of a constant source of carbon, i.e. in CO atmosphere. One of our previous studies (1) revealed that carbon can be removed almost completely from fully saturated Pd-C solid solution by heating in vacuum at 580°C. This low stability of interstitial carbon is remarkable and stands in contrast to the relatively high stability of amorphous or graphite-like surface carbon. A feasible explanation for the high reactivity of interstitial carbon is its atomic dispersion. Literature data (1,6,8-10) indicate that the maximal amount of incorporated carbon is in the range 15-16 at%, i.e. only one-seventh of the octahedral holes in the lattice are occupied. The fact that further incorporation of carbon is not observed irrespective of the presence of "free" holes in the Pd lattice indicates that steric factors are probably not limiting this process. Ziemecki (6) and Stachurski (9) suggested that the determining step is the electronic interaction between palladium and carbon. Strong electronic interaction is a prerequisite for the solution of a gas in a metal, as can be demonstrated by helium, which does not dissolve to a notable extent in any metal. This in spite of the fact that helium atoms are smaller than carbon atoms and no dissociation is required to precede the incorporation (11).

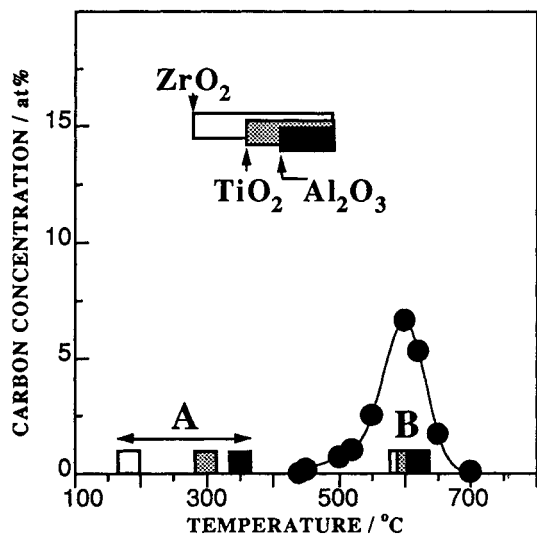


Fig. 7 Temperature range of the existence of saturated Pd-C solid solutions (marked by rectangles) as a function of the kind of support. Temperatures corresponding to beginning of carbon incorporation (A) and total carbon removal (B) are marked by squares. The data for unsupported Pd are presented as solid circles.

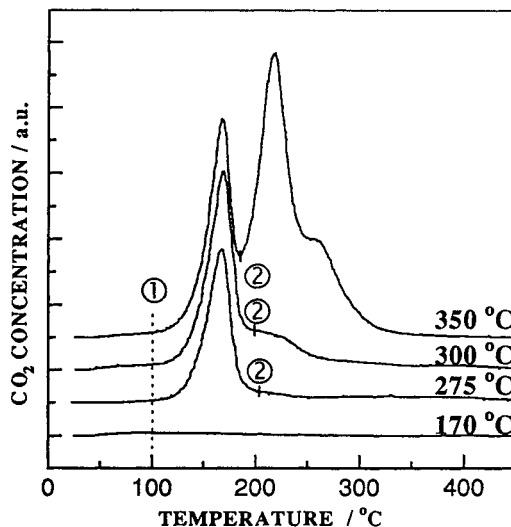


Fig. 8 Evolution of  $CO_2$  originating from oxidation of Pd/ $ZrO_2$  samples containing interstitial and surface carbon. Temperatures of "samples synthesis" (see Fig.3) are marked on curves. XRD analysis was carried out with samples taken at 100°C (points labelled "1") and after first peak of  $CO_2$  evolution (points "2").

Electronic interaction with the conducting electrons of Pd seems to be the major reason for the higher reactivity of interstitial carbon. Separated carbon atoms placed in the octahedral holes of the host lattice possess an electronic state which is expected to be different from that characteristic for surface carbon, which should manifest as a different reactivity towards reduction or oxidation of these carbon species. In order to confirm this assumption, Pd-C/ $ZrO_2$  samples containing different relative amounts of surface carbon were exposed to

hydrogen and oxygen respectively. The samples (prepared as illustrated in Fig. 3) contained the same amount of incorporated carbon (ca. 15 at%) and different amounts of surface carbon were oxidized in 4 vol% O<sub>2</sub> (balance He). The amount of evolved CO<sub>2</sub> was measured by mass spectroscopy. The results (Fig. 8) indicate that the sample prepared at 170°C, i.e. at a temperature slightly lower than that where carbon incorporation is indicated on the thermoanalytical curves, does not show any remarkable evolution of CO<sub>2</sub>. Only a single CO<sub>2</sub> peak occurred during oxidation of sample *b*, prepared by quenching the reaction at 275°C, i.e. at the temperature where carbon incorporation ceased. For samples *c*, *d* and *e* (not shown), the greater the amount of surface carbon was, the larger was the second peak of carbon dioxide evolution. The total amount of carbon in the samples *a-d*, expressed in mg carbon per g of sample, was: *a* - 0.17; *b* - 5.24; *c* - 7.54; *d* - 20.04 and *e* - 73.32. The value of 5.24 for sample *b*, containing only incorporated carbon, indicates that in this sample (30 wt% Pd/ZrO<sub>2</sub>) the interstitial carbon content is 15.5 at%, and that samples *c*, *d* and *e* contain 2.30, 14.80 and 68.08 mg of surface carbon per gram of sample.

X-ray analysis carried out with the samples corresponding to points labelled "1" and "2" (Fig. 8) showed a similar pattern for all samples. Before the first peak of CO<sub>2</sub> evolution (point "1"), the samples possessed a composition corresponding to fully saturated Pd-C solid solution. After the peak (point "2"), only pure palladium was present in the sample, i.e. XRD patterns were identical to those presented in Fig. 4 (patterns "b" and "a", respectively). These results confirmed that interstitial carbon is more reactive than surface carbon and that the reaction with oxygen is complete at ca. 230°C, whereas total oxidation of the surface carbon requires temperatures as high as 330°C (sample *d* obtained at 350°C) or even ca. 380°C (sample *e*, synthesized at 400°C, containing more than 7 wt% surface carbon).

The difference between the reactivity of interstitial and surface carbon is even more distinct for the reaction with hydrogen (4 vol% H<sub>2</sub>, balance He). The mass spectrometric curves of methane formation, (Fig. 9) show that the maximal rate of the reaction of interstitial carbon with H<sub>2</sub> (maximum at ca. 245°C) in sample *d* occurs at a temperature more than 300°C lower than that required for the reaction with surface carbon. These results demonstrate that for palladium samples containing surface- and interstitial carbon formation of methane will occur first by the reaction of hydrogen with the interstitial carbon. Surface carbon seems not to react to methane before the interstitial carbon is totally consumed.

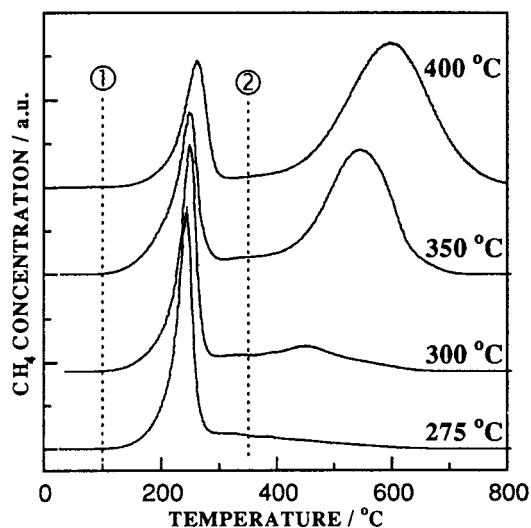


Fig. 9 Evolution of CH<sub>4</sub> produced by reduction of Pd/ZrO<sub>2</sub> samples containing interstitial and surface carbon. Temperatures of samples synthesis are marked on curves. XRD analysis was carried out with samples taken at points labelled "1" and "2".

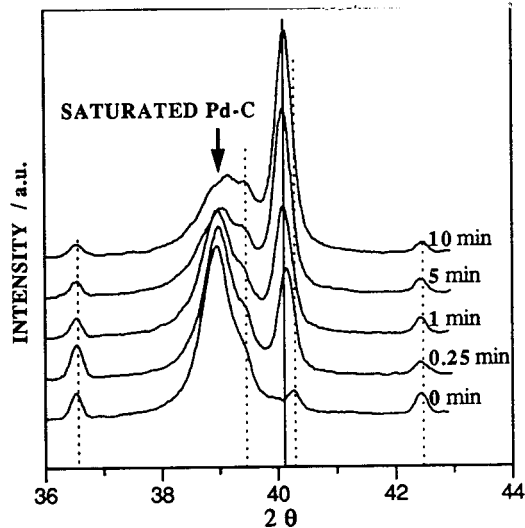


Fig. 10 Change of the position of Pd (111) reflection induced by grinding of Pd-C solid solution with increasing grinding time. Position of the reflections of internal standard (quartz) and Pd are marked by dotted and solid lines, respectively. The position of reflection due to saturated Pd-C solid solution is marked by an arrow.

The high reactivity of the interstitial carbon caused its rapid removal from the Pd lattice and was also indicated by the observation that Pd-C decomposed partially during grinding. A solid solution of carbon in unsupported palladium, with a maximal concentration of carbon ca. 15 at%, was prepared by isothermal decomposition of palladium acetate at 200°C. This synthesis method was chosen because in hydrocarbon atmosphere incorporation of carbon into pure Pd occurs at a much lower temperature. Using e.g. ethylene or acetylene (6,8) it is possible to form a Pd-C solid solution with unsupported Pd with higher carbon concentration than that resulting from the reaction with CO. Saturated Pd-C was carefully mixed with 10 wt% of quartz, used to have an internal standard for XRD measurements, and ground in an agate mortar. X-ray analysis, performed after 0.25, 1, 5 and 10 min of grinding, indicated that carbon was gradually removed from the Pd lattice (Fig. 10). Even after 15 sec of grinding, the reflection characteristic for the Pd-C solid solution decreased, and simultaneously the reflection due to palladium, centered at  $2\theta=40.12^\circ$ , became more prominent. These results show that shear forces and/or heat produced during grinding may suffice to decompose the Pd-C solid solution. Pure palladium formed during grinding was not oxidized, as confirmed by XRD.

### CONCLUSIONS

Palladium catalyses the disproportionation of carbon monoxide at a low temperature according to the equilibrium of the Boudouard reaction. Over palladium supported on various oxides, CO disproportionation occurs at a much lower temperature than over pure, unsupported palladium, indicating that the metal-support interaction plays an important role in this process. The rate of CO disproportionation decreases in the order:  $ZrO_2 > TiO_2 > Al_2O_3$ . With the most active Pd/ZrO<sub>2</sub>, carbon dioxide formation already occurs at ca. 100°C. Carbon, formed by CO disproportionation, begins to incorporate into the palladium lattice already at ca. 180°C, whereas with unsupported Pd this process sets in at ca. 500°C.

With supported catalysts, the Pd-C solid solution starts to decompose in a CO atmosphere at ca. 475°C, and above 600°C, the concentration of carbon in the lattice becomes negligible. The kind of support distinctly influences the temperature at which the incorporation of carbon into Pd starts, but hardly affects the temperature of Pd-C decomposition. For unsupported Pd, the range of the existence of Pd-C is narrow. Incorporation begins at high temperature and the maximal carbon concentration only reaches a value of 6.5 at% at 600°C. Above this temperature, the rate of Pd-C decomposition is higher than the rate of formation, and consequently the carbon concentration decreases. At ca. 700°C, the amount of carbon in unsupported Pd is lower than 0.2 at%.

During continuous heating in CO atmosphere, carbon formed by the Boudouard reaction first incorporates into the Pd crystal lattice, and later, i.e. when maximal carbon concentration is reached (saturation), begins to deposit on the surface. The reactions with oxygen and hydrogen of samples containing a maximal amount of carbon in the lattice and different amounts of surface carbon indicate that interstitial carbon is more reactive. Methane formation from surface carbon seems not to start before the interstitial carbon in the Pd lattice is fully consumed. Interstitial carbon is also more reactive with oxygen than surface carbon, though the difference is smaller.

The high reactivity of interstitial carbon may be explained by its "atomic dispersion" in the crystal lattice, enabling the interaction of carbon electrons with the conducting electrons of the host metal lattice.

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