

Combustion of Methane over Palladium/Zirconia Derived from a Glassy Pd–Zr Alloy: Effect of Pd Particle Size on Catalytic Behavior

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A Pd₂₅Zr₇₅ glassy metal alloy has been activated by controlled oxidation in air, resulting in highly active catalysts for the catalytic combustion of methane. The fully oxidized alloy was reduced in hydrogen at different temperatures prior to catalytic investigations resulting in a catalyst containing metallic palladium and zirconia. The reduced materials showed marked differences in BET surface area and specific surface area of palladium, both decreasing with increasing reduction temperature. The loss of surface area was accompanied by an increase of the palladium crystallite size as evidenced by XRD line broadening measurements. Catalysts reduced at low temperatures were faster reoxidized than catalysts reduced at high temperatures. Changes in the chemical behavior of palladium oxide were indicated by different decomposition behavior and reducibility with hydrogen and methane. Kinetic measurements revealed profound differences in catalytic activity for catalysts in dependence of the reduction temperature. Strong correlations between the catalytic activity and the crystallite size as well as the reducibility of palladium oxide with methane were found for catalysts reduced at different temperatures. The correlation between the reduction with methane and the catalytic performance is explained by a redox mechanism involving palladium oxide. The influence of the particle size on the catalytic activity is attributed to a strong interaction of the Pd-containing phases (Pd, PdO) with zirconia. This (support) effect is suggested to become prominent with decreasing Pd-particle size. © 1997 Academic Press

1. INTRODUCTION

There have been major efforts to investigate the ability of palladium-based materials to catalyze the combustion of methane (1–22). Several aspects of the combustion of methane over palladium are debated in the literature. General agreement exists that palladium oxide is the active phase under reaction conditions in lean mixtures of methane and oxygen. Metallic palladium is oxidized to a certain extent by the reaction atmosphere (9, 16, 19, 22), indicating that the role of metallic palladium is secondary. Whether the surface palladium oxide is more active when

lying on metallic palladium or on palladium oxide is, however, not clear. Massive deactivation is observed during the decomposition of palladium oxide, which is rather attributed to the formation of metallic palladium than the concomitant loss of surface area (11, 18, 19, 22). On the other hand, an increase in activity has been observed if the catalysts were reduced prior to the catalytic testing (2, 5, 16, 22). The enhancement has been attributed to the reconstruction of the palladium oxide crystallites (5). The transformations occurring during reduction and reoxidation have been carefully investigated by various groups (3, 18, 23–27). The particle size of palladium is generally reported to increase upon reduction. The structure sensitivity of the combustion of methane over palladium is extensively discussed. Some groups consider the reaction to be independent of the particle size (2, 6), whereas others regard the influence of the particle size as important (4, 9). However, the rate of the oxidation of palladium itself is accepted to be influenced by the particle size, with small particles showing a higher tendency to be oxidized (2, 4, 5, 25). The possible influence of the particle size is connected with a support effect. The effect of an interaction of the active phase with the support is discussed for the activity as well as for other properties of the catalyst system. According to Cullis *et al.* (2), the support has an impact on the ability of palladium to adsorb oxygen depending on the catalyst loading and a correlation between catalytic activity and the ability to adsorb oxygen has been established. For the temperature-programmed reduction of supported palladium oxide, two different kinds of PdO have been found, differing in the temperature range of reduction (5). The palladium oxide reduced at higher temperatures is attributed to PdO strongly interacting with the support, whereas bulk PdO is reduced at lower temperatures. Similarly, two distinct steps of oxygen evolution are observed for the thermal decomposition of supported palladium oxide (11, 12). Between heating and subsequent cooling, a hysteresis is observed for decomposition and oxidation (11, 18, 19). Zirconia was found to have the largest influence on this hysteresis (18).

As-prepared glassy metals normally exhibit low intrinsic catalytic activity, mainly due to their low surface area. In

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the case of the Pd₂₅Zr₇₅ amorphous alloy used in this work, controlled oxidation in air was found to be essential for high catalytic activity in the combustion of methane (12, 22). The comparison of this catalyst with conventionally prepared catalysts (impregnation, coprecipitation) showed the former to be significantly more active based on the catalyst mass and the Pd surface area. After oxidation, involving several morphological and chemical changes, such as crystallization, segregation, and rise in BET surface area, the catalyst consists of poorly crystalline palladium oxide and monoclinic and tetragonal zirconia. A remarkable property of the catalyst is the very intimate contact of palladium oxide with the support, which is a consequence of the amorphous state of the precursor and the exceptional mixing of the constituents. Another important advantage of catalysts derived from glassy metal alloys is the negligible amount of impurities and residuals as compared to catalysts prepared from salt precursors. Severe problems were reported to originate from the use of chloride and nitrate (5, 7, 15).

The purpose of this work is to clarify the effect of the pre-reduction of palladium oxide supported on zirconia on the catalytic activity for the complete oxidation of methane. In combination with the inquiries concerning the catalytic activity of these catalysts, we will aim to correlate the catalytic behavior of zirconia supported palladium with the morphological and chemical properties of the catalyst before and after reduction.

2. EXPERIMENTAL

2.1. Catalyst Precursor

The amorphous alloy used as catalyst precursor was prepared from the premixed melt of the pure constituents by rapid quenching using the technique of melt spinning. The resulting ribbons were ground into flakes of 200–400 μm size. The as-prepared amorphous alloy with the nominal composition Pd₂₅Zr₇₅ was activated by oxidation in air at temperatures of 553 and 623 K, respectively, until full oxidation was accomplished. The BET surface area of the oxidized catalyst amounted to 24.4 $\text{m}^2 \text{g}^{-1}$. The resulting PdO/ZrO₂ catalyst prepared by oxidation at 623 K is referred to as *Pd*, and the catalyst derived from this sample by reduction are additionally labeled with the temperature of reduction (*Pd-T_{red}*).

2.2. Physicochemical Characterization

X-ray analysis was carried out on a Siemens D5000 powder X-ray diffractometer in a step mode (step size 0.01° and 0.3 s) using Ni-filtered CuK α radiation (35 mA, 45 kV). The patterns obtained were compared with JCPDS data files (JCPDS Mineral Powder Diffraction Data Files, Park Lane, PA). The mean crystalline size of metallic palladium was calculated from the Pd(111) reflection using the Scherrer

equation with $K=0.9$ and the half-maximum line width correction for Gaussian line profiles (28).

Thermoanalytical investigations (DTA/TG) were carried out at atmospheric pressure on a Netzsch STA 409 thermoanalyzer equipped with PtRh10/Pt thermocouples and Pt crucibles (decomposition) and on a Mettler TA 2000C (reduction and reoxidation). The decomposition of PdO of the fully oxidized samples was performed under air with a heating rate of 10 K min^{-1} . The reduction prior to the determination of the crystallite size and the reoxidation was carried out by heating under pure H₂ (flow rate 40 ml min^{-1}) with 10 K min^{-1} from room temperature to the temperature of reduction using 100 mg oxidized catalyst. After quenching, the samples were additionally heated to 673 K at a heating rate of 10 K min^{-1} under pure Ar (40 ml min^{-1}) to decompose possibly formed PdH_x. The reoxidation of the reduced samples was performed under air (flow rate 40 ml min^{-1}) with a heating rate of 10 K min^{-1} .

The temperature-programmed reduction with hydrogen (TPR) and the temperature-programmed oxidation (TPO) of the samples were performed in a fused-quartz microreactor (6.32 mm o.d. and 4 mm i.d.). The samples were treated with 5% H₂ in a balance of Ar (75 ml min^{-1} , STP) for the TPR and with 5% O₂ in a balance of Ar (50 ml min^{-1} , STP) for the TPO with a heating rate of 10 K min^{-1} . The reaction was monitored by a thermal conductivity detector (TCD). The temperature-programmed reduction of the catalysts with methane was carried out in the same microreactor with a reduction atmosphere containing 1% methane in a balance of He (total flow 300 ml min^{-1}) and a heating rate of 10 K min^{-1} . The composition of the gas mixture leaving the reactor was analyzed with a mass spectrometer (Balzers GAM 400).

Nitrogen adsorption/desorption isotherms were measured at 77 K using a Micromeritics ASAP 2000 instrument. Prior to the measurements, the samples were degassed in vacuum at 423 K for 1 h. The surface area (S_{BET}) was calculated in a relative pressure range p/p_0 between 0.05 and 0.25, assuming a cross-sectional area of 0.162 nm^2 for the nitrogen molecule.

The specific palladium surface area was determined by CO chemisorption measurements. The samples were reduced at room temperature with a mixture of N₂ and H₂ until the observed exothermic reaction was accomplished. Subsequently, the samples were heated under pure hydrogen to the reduction temperature (except the sample reduced at room temperature) and kept for 1 h under these conditions. The reduced samples were then treated with pure N₂ at 623 K (373 K for the sample reduced at room temperature). CO chemisorption experiments were carried out at room temperature as described in (12). Studies of the CO adsorption using diffuse reflectance FTIR spectroscopy revealed that on a catalyst prepared from Pd/Zr amorphous alloys bridge-bound CO was the prevalent surface species

in a pure CO atmosphere (29). Based on these findings, the specific palladium surface area was calculated assuming a stoichiometric factor of 2 for the adsorption of CO on palladium and a cross-sectional area of 0.0787 nm^2 for the palladium atom (30).

2.3. Catalytic Tests

Steady-state kinetic measurements for the combustion of methane were carried out in a continuous fixed-bed microreactor (6.32 mm o.d. and 4 mm i.d.), operated at atmospheric pressure, using a mass spectrometer (Balzers GAM 400) for gas analysis. Comparative catalytic tests with oxidized as well as with prerduced samples were performed using an amount of oxidized catalyst obtained from 250 mg amorphous alloy under a reactant flow rate of 300 ml min^{-1} (STP). The reaction gas mixture, premixed from pure gases without further purification, consisted of 1% CH_4 (99.995%) and 4% O_2 (99.999%) in a helium balance (99.998%). Prior to kinetic tests, the catalyst oxidized in air was conditioned in the reaction gas mixture for 1 h at room temperature. After conditioning, the temperature was increased stepwise within a range of 450–800 K. The catalyst temperature was measured by a thermocouple at the center of the bed. Methane conversion was calculated on the basis of a carbon balance including CO_2 and CH_4 . In a previous study (12), it was shown that no interparticle mass transport limitations have to be taken into account for the parameter range investigated. Conventional tests for pore diffusion control could not be made with catalysts prepared from amorphous alloys. However, tests with two reference catalysts in (12) revealed that internal diffusion was not controlling the overall reaction rate.

Reduction of the catalysts prior to catalytic testing was performed *in situ* by heating the samples under a hydrogen-helium stream (total flow 300 ml min^{-1} , 95% He, 5% H_2) with 10 K min^{-1} to the respective reduction temperature. The reduced samples were quenched under pure He (total flow rate 285 ml min^{-1}), heated to 623 K and kept at this temperature for 0.5 h. After changing to the reaction gas mixture at room temperature, catalytic tests were performed as described above.

3. RESULTS

3.1. Influence of Reduction Temperature on Morphology

A catalyst prepared by oxidation of an amorphous $\text{Pd}_{25}\text{Zr}_{75}$ alloy oxidized at 623 K in air was the starting material for the following investigations.

The development of the mean crystallite size of metallic palladium present after reduction and subsequent exposure to air at room temperature is depicted in Fig. 1 as a function of the reduction temperature. For reduction temperatures below 600 K, the mean crystallite size remained between 5–6 nm. For temperatures exceeding 600 K the crystallite

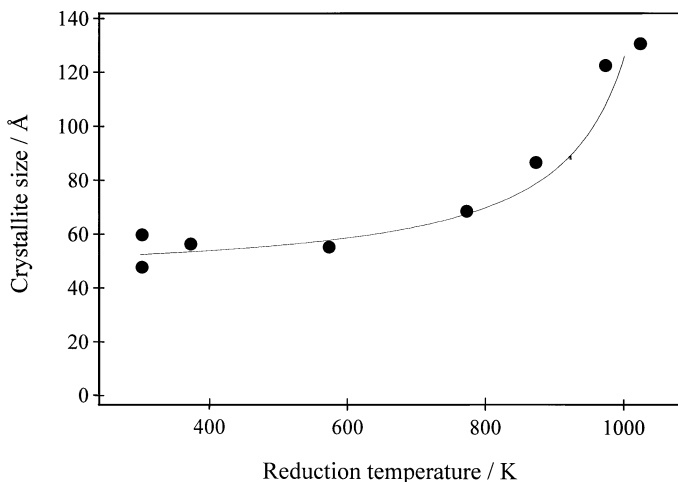


FIG. 1. Mean crystallite size as a function of the reduction temperature as measured by XRD line broadening ($\text{CuK}\alpha$) of the (111) reflection of palladium; calculation based on the Scherrer equation with $K = 0.9$ (unknown form of the crystallites, full half-maximum line width).

size increased up to 14 nm within the temperature range investigated. At this temperatures sintering of metallic palladium is expected to occur. This assumption is supported by investigations made on the atomic mobility, expressed by the Tammann temperature, and on the wetting behavior of metals on oxidic supports (26, 31). The Tammann temperature, estimated as the half of the bulk melting temperature (31), is 914 K for metallic palladium. Around this temperature, a strong increase in the crystallite size of palladium is observed in Fig. 1. An increase in particle size results in a smaller interface between palladium and the support. Thus, a possible influence of the support on the behavior of palladium becomes less significant.

The influence of the reduction temperature on the textural properties of the catalysts was followed by nitrogen adsorption and CO chemisorption experiments. Upon reduction and subsequent catalytic testing, the BET surface area decreased with increasing reduction temperature (Fig. 2). After testing, the average pore diameter ($d_p = 4V/A$) was 2.3 nm for *Pd-293*, 3.1 nm for *Pd-573*, 2.6 nm for *Pd-873*, and 3.9 nm for *Pd-973*. Small pores are obviously eliminated, thus lowering the total surface area and shifting the average pore diameter toward higher values.

The decrease of the BET surface area is accompanied by a concomitant loss of specific palladium surface area (Fig. 3). This observation confirms the increasing particle size of metallic palladium with increasing reduction temperature. Assuming a shape-retaining growth of the Pd particles and the total amount of palladium present at the surface of the catalyst particles to be constant, the surface area should be proportional to the inverse of a characteristic length of the particle, e.g., mean particle size. This relation cannot be confirmed with our experimental data. In light of the

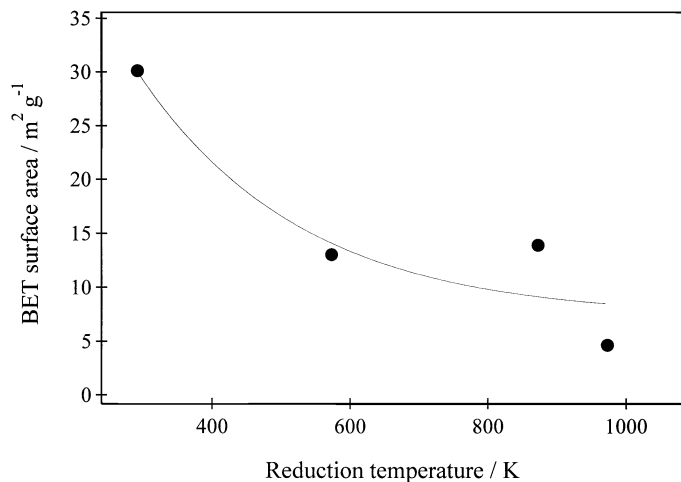


FIG. 2. BET surface area as a function of the reduction temperature (samples after catalytic testing). Nitrogen adsorption, $S_{N_2} = 0.1620 \text{ nm}^2$.

results of the BET surface area measurements, we suggest that a certain amount of palladium becomes inaccessible to the gas phase by the elimination of small pores, and thus the assumption of a constant amount of palladium on the surface seems to be inadequate.

3.2. Chemical Behavior of the Reduced Catalysts

The reoxidation behavior of reduced catalysts was studied by means of thermoanalytical methods. PdO/ZrO₂ obtained by oxidation of the Pd₂₅Zr₇₅ amorphous alloy at 623 K was reduced by hydrogen at different temperatures and subsequently heated in Ar at 623 K to decompose possibly formed palladium hydrides. TA-MS measurements performed after reduction showed that the catalysts is fully reduced for all reduction temperatures. The reduced mate-

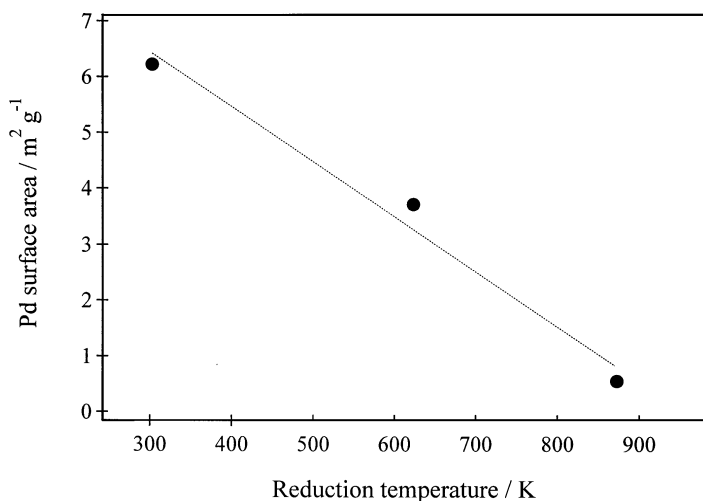


FIG. 3. Specific palladium surface area as a function of the reduction temperature. CO adsorption, $S_{Pd} = 0.0787 \text{ nm}^2$; stoichiometric factor, 2.

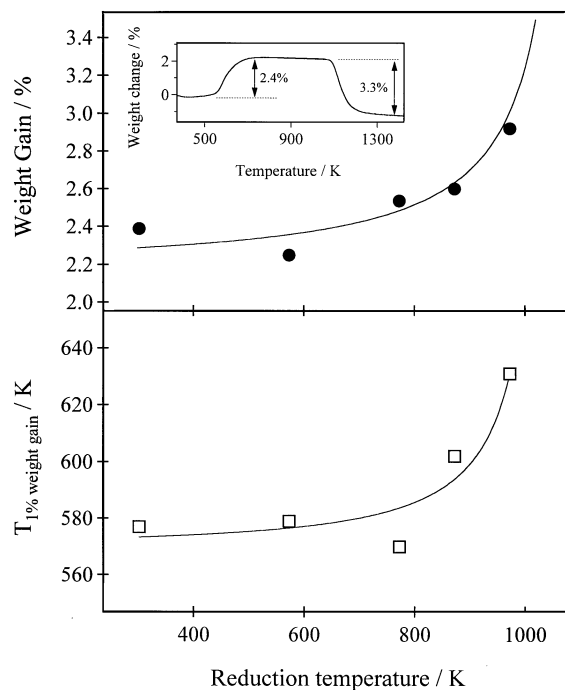


FIG. 4. Reoxidation behavior in air of the previously reduced catalyst investigated by TG (catalysts exposed to room atmosphere after reduction); \square , $T_1\%$ weight gain-values; \bullet , total weight gain during controlled oxidation (excluding uptake at room temperature). Conditions: air flow rate, 40 ml min^{-1} (STP); heating rate, 10 K min^{-1} ; sample weight, 100 mg.

rials were exposed to air at room temperature which was accompanied by a marked exothermic effect (up to 50 K). The reoxidation behavior of the catalysts upon increasing the temperature by 10 K min^{-1} under O₂/Ar is illustrated in Fig. 4. The inset in the upper part of Fig. 4 depicts the general course of the reoxidation and the decomposition of palladium oxide at higher temperatures. It clearly shows that the amount of oxygen released during the decomposition is larger than the amount of oxygen taken up in the temperature range 500–800 K. This observation is explained by the uptake of a certain amount of oxygen during the contact of the samples with the oxidizing atmosphere at ambient temperature, which is additionally supported by the exothermicity found at room temperature. The upper part of Fig. 4 (\bullet) shows the final weight gain measured by TG for the catalysts reduced at different temperatures. The comparison with the stoichiometric weight gain due to the formation of PdO (3.25%) is a measure of the amount of oxygen consumed during exposure of the reduced catalysts to air at room temperature. For samples reduced at 573 K (*Pd-573*), the oxygen taken up at room temperature equals ca. 30% of the stoichiometric quantity necessary for the total oxidation of Pd to PdO, whereas the value amounts to ca. 10% for sample *Pd-973*. TPO experiments of *Pd-573* after *in situ* reduction starting from 232 K revealed an immediate oxygen uptake corresponding to 8% of the theoretical uptake,

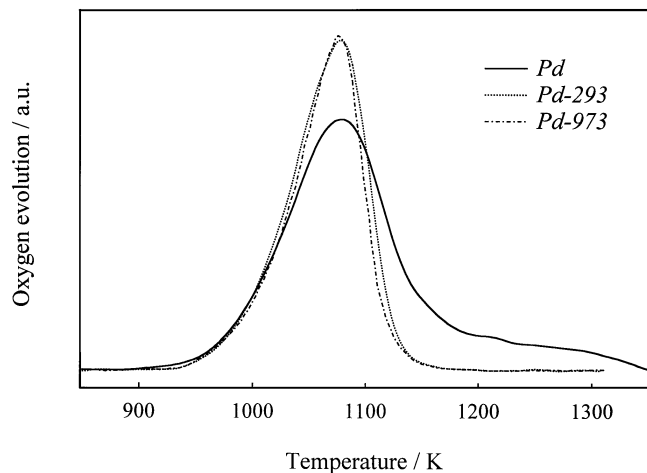


FIG. 5. Decomposition of PdO of catalysts reduced at different temperatures (*Pd-293*, *Pd-973*) followed by reoxidation and an unreduced catalyst (*Pd*). Conditions: Ar flow rate, 30 ml min⁻¹ (STP); heating rate, 10 K min⁻¹; sample weight, 100 mg.

followed by a second peak at 593 K, where Pd is oxidized to PdO (not shown).

The rate of oxidation, represented as the temperature at which 1% weight gain were achieved (lower part of Fig. 4, □), shows a similar dependence on the reduction temperature. Catalysts reduced at low temperatures (400–600 K) are faster reoxidized than catalysts reduced at temperatures exceeding 800 K.

As another property depending on the temperature of reduction, the decomposition of PdO under air is depicted in Fig. 5. The same temperature for the maximum oxygen evolution is observed for the unreduced catalyst (*Pd*) and the catalysts reduced at different temperatures (*Pd-293*, *Pd-973*). However, the *Pd* catalyst shows in addition a significant amount of palladium oxide decomposing at markedly higher temperatures (1150–1350 K), which cannot be detected for the previously reduced catalysts (full decomposition in the range 900–1150 K). The findings indicate that the unreduced catalyst contains a palladium oxide species which is more stable against decomposition. Interestingly, reduction at room temperature is sufficient to eliminate the contribution of PdO decomposed in the temperature range 1150–1350 K. Reduction at 773 K and reoxidation have been repeated twice to investigate the possibility of further affecting the decomposition behavior, but no major differences have been found comparing the decomposition after the first and the second reoxidation.

The temperature-programmed reduction (TPR) with hydrogen of previously reduced and reoxidized catalysts is shown in Fig. 6. As a reference for the unreduced catalyst, an amorphous alloy oxidized at 553 K equivalent to the alloy oxidized at 623 K was used. The reduction of palladium oxide started well below room temperature and continued up to 330 K for all samples. The reduction of the un-

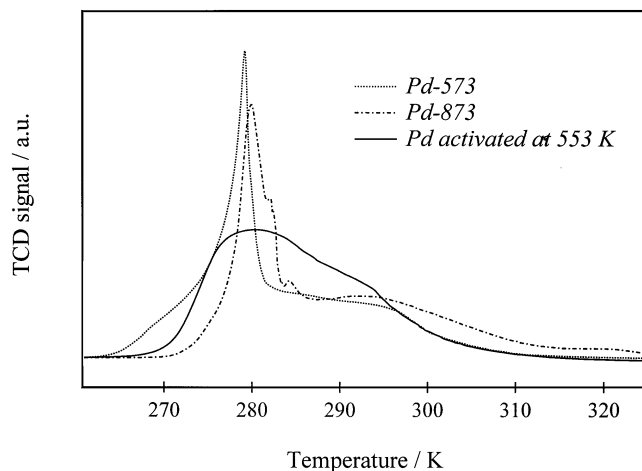


FIG. 6. Temperature-programmed reduction (TPR) with 5% H₂ in Ar of an unreduced catalyst and of catalysts reduced at different temperatures. Conditions: total flow rate, 75 ml min⁻¹ (STP); heating rate, 10 K min⁻¹.

treated catalyst occurred in a wide temperature range with no clear maximum. For previously reduced catalysts, the reaction proceeded in two distinct steps. Both samples (*Pd-573* and *Pd-873*) showed a prominent peak around 280 K and a weaker one around 295 K. The decomposition of the palladium hydrides formed during reduction occurred in the range 353–373 K (not shown). Due to the high rate of the reduction, an exact differentiation of the reducibility by hydrogen was difficult to achieve.

Distinct differences are observed upon reduction of the catalysts with methane (Fig. 7). Compared to the reduction with hydrogen, the reaction of methane with palladium oxide occurs at higher temperatures (450–700 K) and pronounced differences in the course of the reaction

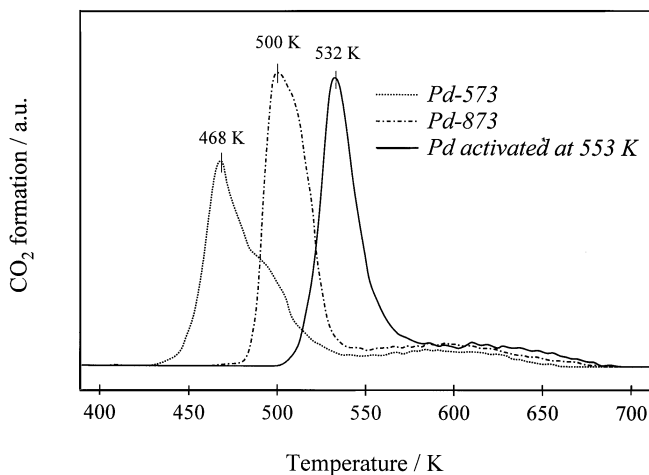


FIG. 7. Reduction with 1% CH₄ in He of an unreduced catalyst and of catalysts reduced at different temperatures after reoxidation. Conditions: total flow, 300 ml min⁻¹ (STP); heating rate, 10 K min⁻¹; sample weight, 50 mg.

are discernible for all catalysts. Furthermore, the reducing agent is also a constituent of the reaction mixture and possible interactions of the reaction atmosphere with the catalyst are of special interest. The results presented in Fig. 7 fit well with the previous experiments, showing palladium oxide to become more reactive after prereduction. The catalyst reduced at the lower temperature (*Pd-573*), after reoxidation, is reduced most rapidly by methane. Clearly visible is a shoulder around the temperature of the peak maximum of the catalyst reduced at 873 K. The temperature necessary to reduce the untreated catalyst is higher than for the prereduced catalysts. An interesting observation made with all catalysts is that a small amount of CO₂ was produced at temperatures in the range 600–700 K. The amount of this CO₂ was almost the same for all catalysts.

3.3. Effect of Pretreatment on the Catalytic Performance

In the previous paragraphs, the morphological and chemical properties of the catalysts after reduction and reoxidation have been investigated. The observed differences are mostly related to bulk properties and cannot, except for the surface area developments, be referred directly to the state of the surface. However, the catalytic activity represented as the steady-state methane conversion vs. the temperature depicted in Fig. 8 also reveals significant variations in dependency of the reduction temperature. Catalysts reduced at low temperatures (293 K and 573 K) are more active than the untreated catalyst, whereas the catalyst reduced at 973 K is less active. The changes in activity as expressed by the temperature necessary to obtain 50% conversion, $T_{50\%}$, lie within a range of almost 100 K. XRD measurements of the materials after catalytic testing showed that the catalysts, previously reduced *in situ*, are oxidized by the

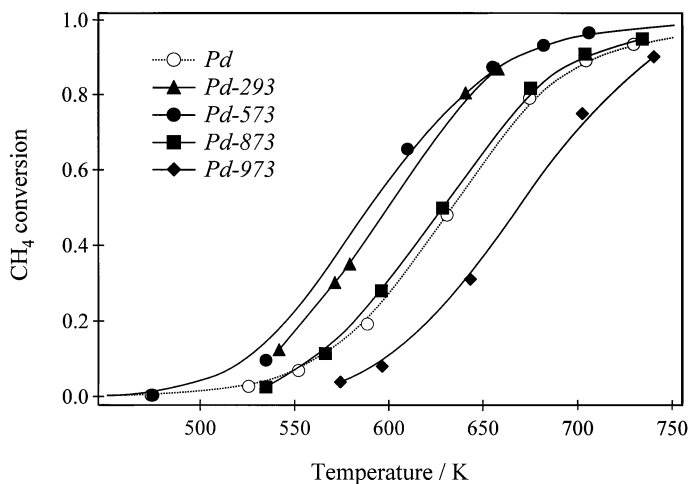


FIG. 8. Comparison of methane oxidation activities of an unreduced catalyst (*Pd*) and of catalysts reduced at different temperatures. Amount of catalyst is based on 250 mg of amorphous alloy. Reactant gas composition: 1% CH₄, 4% O₂, He (balance); total flow, 300 ml min⁻¹ (STP).

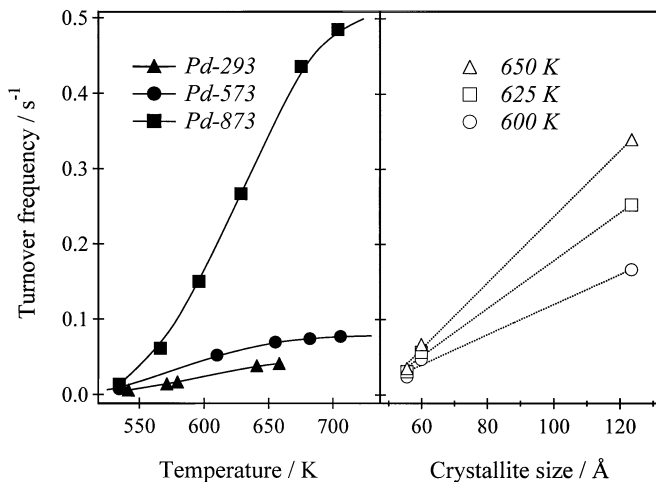


FIG. 9. Turnover frequency vs. temperature for catalysts reduced at different temperatures and crystallite size at different reaction temperatures. TOF calculations are based on the specific surface area measurements assuming $S_{Pd} = 0.0787 \text{ nm}^2$; stoichiometric factor, 2.

reaction atmosphere (only PdO phase peaks observable). An enhanced activity therefore cannot be attributed to a higher activity of metallic palladium. The differences in activity shown in Fig. 8 are due to the intrinsic properties of the catalysts and are not explainable by different amounts of metallic palladium. Note that the conversion of methane becomes significant (i.e., higher than 10%) at temperatures above the maximum peak temperature for the reduction of palladium oxide with methane for the respective catalysts. The order of activity for the combustion of methane correlates well with the order of the reducibility of palladium oxide with methane.

More conclusive information concerning the influence of the crystallite size emerges from the determination of the specific turnover frequency referred to the number of palladium atoms exposed, which is shown as a function of temperature for catalysts reduced at different temperatures and crystallite size at different reaction temperatures in Fig. 9. The intrinsic activity of a palladium atom increases with increasing reduction temperature, i.e., with increasing crystallite size (Fig. 1). The crystallite size dependence of the intrinsic activity is based on the assumption that the specific surface area of palladium after reduction, on which the calculation of the turnover frequency is based, is a direct measure of the number of active sites present in the catalyst after oxidation under reaction conditions. Although this assumption may not be absolutely valid, the absence of any significant morphological changes after catalyst testing at a specified temperature supported this assumption.

4. DISCUSSION

The complete oxidation of methane over palladium/zirconia is Pd crystallite size dependent as indicated by

Fig. 9. The prereduction of catalysts in a wide range of temperatures (293–873 K) results in an enhanced activity compared to the corresponding unreduced catalyst. The major morphological change occurring during the reduction is the growth of the Pd crystallites (Fig. 1) at high reduction temperatures. This effect is well known (18, 23–27), and the crystallite size determined by means of XRD line broadening (5–15 nm) is within the range of that of other supported Pd catalysts reported in the literature (4–13 nm (23), 3–35 nm (24), 2–20 nm (27), 4–26 nm (2), 2–39 nm (6), 2–77 nm (5), 2–10 nm (7), 1–10 nm (13), and 4–12 nm (14)). The concomitant loss of specific surface area of palladium as a function of the reduction temperature (Fig. 3) is due to the larger particles in combination with the decreasing BET surface area (Fig. 2). Our results clearly indicate that the reduction is an efficient tool for controlling the morphological properties of the catalysts before use.

The activity of PdO/ZrO₂ catalysts depends on the interaction between the active Pd phase and zirconia. The larger the interface between the (oxidized or metallic) noble metal and zirconia, the more prominent this interaction is thought to be. An increasing particle size results in a smaller impact of the zirconia on the chemical behavior of palladium or palladium oxide. A good dispersion of palladium or palladium oxide, giving an intimate contact with the support, leads to a stronger tendency for palladium to be oxidized and to stabilize palladium oxide against decomposition and reduction (2, 3, 5, 11, 12, 25). In combination with the results of the crystallite size measurements, we can corroborate this behavior by the reoxidation (Fig. 4), decomposition (Fig. 5), and reduction experiments performed (Figs. 6, 7). Interestingly, a similar picture emerges for the mean crystallite size (Fig. 1) and the weight gain (Fig. 4) as a function of the reduction temperature. These findings indicate that smaller Pd crystallites are oxidized to a higher extent at room temperature compared to larger crystallites. The composition of the phases formed during exposure of palladium to air at room temperature were not investigated. However, the results cannot be explained simply by the fact that oxygen is adsorbed on the surface of metallic palladium. The correlation between the uptake and the specific surface area (Fig. 3) does preclude this. In fact, the oxygen uptake follows well the development of the crystallite size, which indicates a link between the oxygen uptake at room temperature and the metal–support interaction. This influence remains during oxidation, leading to a faster formation of palladium oxide in catalysts with higher Pd-dispersion.

The stabilizing effect of zirconia on palladium oxide is well apparent for the decomposition of palladium oxide (Fig. 5). In agreement with the literature (12, 32, 33), we interpret the stabilization of palladium oxide for the unreduced catalyst up to 1350 K as an effect of the very intimate contact of this phase with zirconia. The intimate mixture of palladium oxide and zirconia, obtained by the oxidation of

a glassy metal, results in a high dispersion and in marked differences for the decomposition of PdO before and after reduction/reoxidation. The stabilizing effect of the zirconia support also influences reactions of the solid catalyst with gaseous components, as further demonstrated by the reducibility of palladium oxide with hydrogen (Fig. 6) and methane (Fig. 7). The reduction of palladium oxide with methane especially reveals an interesting behavior of the catalysts. The correlation with the catalytic activity indicates that a direct link between the reducibility of palladium oxide with methane and the activity of palladium oxide for the combustion of methane exists. This connection points toward a mechanism involving strongly bound oxygen. The nature of this oxygen cannot be assigned unambiguously. It could be either lattice or strongly chemisorbed oxygen. The reaction involving PdO has previously been proposed (11, 14, 16, 34), but no clear experimental evidence has been given to support this suggestion. A redox or Mars & van Krevelen-type mechanism includes the reduction of palladium oxide to Pd by methane and subsequent oxidation of the palladium by oxygen. The need for reoxidation of palladium let Farauto *et al.* (11) exclude the possibility of a redox mechanism above the PdO decomposition temperature. However, a reaction mechanism of this type is possible for temperatures below the temperature of the decomposition of palladium oxide. A redox mechanism involving PdO explains very well previous results found in literature. Oxygen containing palladium phases are a necessary requirement for catalytic activity, although the degree of oxidation is unclear. Burch *et al.* (16) stated that about four monolayers of oxygen are indispensable for good catalytic performance of palladium catalysts, whereas a continuing oxidation does not lead to better catalysts. A redox mechanism involving the surface and few submonolayers is in good agreement with these results. Since consecutive reoxidation of the surface is crucial for this type of mechanism, we are therefore confronted with the counteracting need for simultaneous ease of reduction and oxidation. Near the temperature of decomposition, a change in the rate-determining step of the overall combustion reaction should be detected, as it is indeed reported in literature (1, 2). Furthermore, the activity of palladium-based catalysts has to decrease drastically under conditions where palladium oxide is not stable. A redox reaction pathway therefore is a sound explanation for the loss of activity during PdO decomposition.

Focusing on the role of lattice oxygen, the complete oxidation of methane has been studied over a palladium/zirconia catalyst containing ¹⁸O labeled palladium oxide (35). A substantial amount of labeled reaction products such as CO₂ (with masses 46 and 48) and H₂O (with mass 20) have been detected upon reaction of pulses of the reaction mixture, consisting of methane and oxygen (mass 32) in a ratio CH₄:O₂ = 1:4, with the catalyst. Since isotope exchange of both molecular oxygen and carbon dioxide took place to

a large extent, the occurrence of a redox mechanism could be shown only for a temperature of 573 K. The amount of CO₂ produced by a redox mechanism was estimated to be at least 20%. Therefore, in combination with the results presented in this work, strong evidence exists that the combustion of methane over palladium/zirconia catalysts is influenced by a redox or so-called Mars & van Krevelen-type mechanism.

We resume that the catalytic combustion of methane over zirconia supported palladium is structure sensitive in terms of a dependency of the activity on the crystallite size. Profound changes in the chemical behavior caused by pre-reduction were found to have a direct impact on the catalytic performance, giving rise to the activity dependence on the reduction temperature. Because of the use of glassy metals, we can virtually exclude the removal of residuals or impurities to be responsible for the enhancement of the catalytic activity. The correlation between activity and bulk properties is proposed to be based on a contribution of a redox mechanism involving palladium oxide. The influence of the particle size, as shown, can be understood in terms of two major contributions. The activity of sites exposed on the surface of large palladium oxide particles is higher than the activity of sites on smaller particles. This is attributed to a strong support effect and illustrated by the dependence of the TOF values on the reduction temperature (Fig. 9). The overall performance of the catalyst, however, is a result of the specific surface area and the specific activity of the active sites, both properties being opposingly influenced by the particle size. The optimal catalytic activity for the catalysts used is achieved by reduction at the lowest possible temperature.

5. CONCLUSIONS

The reduction of an oxidized glassy metal with the composition Pd₂₅Zr₇₅ is shown to be an interesting possibility to prepare palladium/zirconia catalysts highly active for the complete oxidation of methane. The morphological changes occurring during reduction have a strong influence on both the chemical and catalytic properties of the catalyst. The methane combustion was found to be dependent on the palladium crystallite size. The turnover frequency decreases with decreasing crystallite size. Further correlations between the activity and decomposition and the reducibility of palladium oxide with hydrogen and methane indicate a significant contribution of a Mars & van Krevelen type reaction mechanism, which has been independently confirmed by isotope-labeling experiments (35). A strong influence of zirconia, stabilizing palladium oxide and therefore reducing the catalytic performance in the temperature range investigated, can be diminished by reduction at ap-

propriate temperatures. The counteracting influences of the particle size and specific surface area of palladium on the overall conversion have to be optimized to attain best catalytic activity.

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