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Mechanism of the partial oxidation of methane to synthesis gas over Pd

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The partial oxidation of methane to synthesis gas has been studied in an isothermal continuous flow reactor operated with the phases in plug flow, using a silica-supported palladium catalyst. The reaction mechanism involves the sequential combustion and reforming of methane. The catalyst bed is not uniform in terms of the composition of the palladium phase. The implications for investigations using a pulse apparatus are discussed. Finally, large palladium crystallites readily grow carbon filaments.

Keywords: partial oxidation, synthesis gas, methane, palladium, carbon filaments

1. Introduction

Synthesis gas is the feedstock for large volume processes such as methanol and Fischer–Tropsch synthesis [1,2]. The partial oxidation of methane to synthesis gas currently attracts increasing attention as an alternative to the steam reforming of methane [3–10].

The partial oxidation of methane readily proceeds over both non-noble and noble metal catalysts [11–27]. The reaction mechanism is still debated. Several authors claim that certain catalysts promote the selective oxidation of methane to carbon monoxide and hydrogen (direct route) [14,15,20,21,23–26]. However, other studies state that synthesis gas is the product of the sequential combustion and reforming of methane (indirect route) [11–13,16,17–19].

The elucidation of the reaction pathway is of vital importance for the design of the industrial process: assuming complete oxygen conversion, we estimated an adiabatic temperature rise at 298 K of about 1900 and 400 K for the indirect route and direct route, respectively (thermodynamic data were taken from literature [28]). Consequently, severe heat management problems have to be taken into account if the indirect reaction pathway predominantly contributes to the conversion of methane to synthesis gas.

Evidence for CO and H_2 being the secondary products is available for the nickel-catalyzed reaction: essentially zero CO selectivity is observed at low methane conversion levels. Moreover, a steep temperature profile is present in the catalyst bed due to the sequential exothermic combustion and endothermic reforming of methane [11,17–19].

While consensus seems to have been reached for the nickel-catalyzed reaction, the remaining unanimity predominantly concerns the reaction pathway over noble metals. Several studies state that the direct route is the main pathway over Ru/TiO_2 [20], and supported Pt [21,23], Pd [22], Rh [24–26] catalysts. In contrast, the Oxford group suggested that the formation of synthesis gas over the same noble metals mainly proceeded via the indirect route [12,13]. However, no experimental evidence for this postulate is available to date. The aim of the present study was to contribute to a better fundamental understanding of the reaction pathway over noble metal catalysts. In the current paper we present the results obtained with supported palladium catalysts. Except for the mechanistic aspects, we briefly report on the deposition of carbon, too. In comparing different noble metal catalysts, we plan to present our results obtained with a Ru/TiO_2 catalyst in the near future.

A number of experimental pitfalls seems to complicate rapid progress in the field of the elucidation of the reaction pathway of the partial oxidation of methane to synthesis gas.

In the first place, the contribution of the indirect route can bring about a steep temperature profile even in small laboratory reactors, which easily leads to erroneous conclusions concerning the mechanism, as has previously been discussed [16,17,19]. Therefore, the present investigations were conducted under strictly isothermal conditions.

Secondly, TAP experiments may also contribute to a better understanding of the reaction mechanism under steady-state conditions provided [29] (i) the conversion of the reactants is sufficiently low, (ii) the composition of the catalytically active phase is uniform along the catalyst bed, and (iii) the composition of the catalyst surface is representative for the situation under steady-state conditions. The third requirement is best fulfilled [29] with the simultaneous pulsing of labelled reactants under steady-state operation. Unfortunately, with the partial

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oxidation of methane the conversion of oxygen reportedly is always very high [21,24–26]. As a consequence, the occurrence of sequential reactions in the catalyst bed cannot be excluded, rendering identification of the primary products highly difficult. In addition, it is highly questionable whether the composition of the catalytically active phase is uniform along the catalyst bed. Previously conducted experiments using a nickel catalyst demonstrated that the gas atmosphere was oxidizing at zero conversion, but reducing at high conversion [30]. As a consequence, the relative stabilities of the metallic and oxidic phase were shown to depend on the conversion level. In addition, the deposition of carbon on the catalyst was observed [31]. The simultaneous presence of oxidic, metallic, and carbidic and/or graphitic phases is one of the reasons why the chemistry of the partial oxidation of methane is so complicated. Analogously to the nickel catalyst, preliminary results of in situ ellipsometry and in situ high temperature X-ray diffraction experiments using a palladium catalyst indicated that the phase composition of the palladium in the catalyst bed was not uniform along the catalyst bed. Since the requirements for meaningful TAP experiments were not met we decided to conduct the present investigations in a conventional continuous-flow reactor.

Finally, with a Pt gauze the formation of synthesis gas in the presence of oxygen in the product gas at very short contact times was presented as a strong indication that CO and H_2 were the primary oxidation products [22,23]. However, the slip of oxygen owing to deviation from plug-flow behavior as predicted by the Péclet number was not taken into account. In contrast, in the present study we verified that the measurements were conducted under conditions fulfilling the Gierman criterion to ensure reactor plug-flow behavior [32,33].

2. Experimental

2.1. Catalysts

The catalysts PS (small Pd crystallites) and PL (large Pd crystallites) were prepared by ion-exchange. 9.6 g of silica powder (OX-50, Degussa, 50 m^2/g) was suspended in 150 ml demi-water. The pH of the suspension was raised to a value of 9 by the addition of an aqueous solution of ammonia (Lamers and Pleuger). Subsequently, 9.09 g of a 4.4 wt% solution of tetramine palladium(II) nitrate in water (Johnson Matthey) was added dropwise to the suspension. The volume of the suspension was doubled by the addition of demi-water, and the suspension was stirred for 1 day. Subsequent to filtration, the residue was rinsed with 50 ml of demi-water and dried at room temperature under a stream of nitrogen for 3 days.

A sieve fraction of the fresh catalyst between 150 and 425 micron was placed into a quartz reactor. The sample was flushed in helium at room temperature for 30 min. Subsequently, the temperature was raised from room temperature to 573 K at a rate of 5 K/min, and flushed for 30 min. Subsequently, the temperature was enhanced to 673 K at a heating rate of 5 K/min. A catalyst containing rather large palladium particles (PL) was obtained by raising the temperature from 573 to 673 K in a stream of 10 vol% hydrogen in helium. A catalyst with relatively small crystallites (PS) was prepared by raising the temperature to 673 K in helium. Subsequently, the helium stream was replaced by a mixture of 10 vol% hydrogen in helium. The temperature of both catalysts was kept at 673 K for 4 h. The reduced catalysts were cooled down to room temperature. The thus obtained catalysts were slightly blue to greyish. The palladium crystallites were too small to be detected by means of transmission electron microscopy (TEM) using a Philips EM 420. Titration experiments revealed that both catalysts contained about 2 wt% Pd/SiO_2. Catalyst PL contained palladium crystallites of about 5 to 10 nm as determined with TEM. X-ray diffraction displayed the presence of metallic palladium only: the reduction temperature employed was probably too low for the pronounced formation of palladium silicide [34,35]. X-ray diffraction (XRD) measurements were performed in a Philips powder diffractometer placed on a Philips PW 1140 X-ray generator with Fe $K\alpha_{1,2}$ radiation ($\lambda = 1.93735$ Å).

A 0.5 wt% Pd/SiO_2 was also prepared by ion-exchange: 1.15 g of the palladium(II) nitrate solution in 30 ml demi-water was added dropwise to 10 g of silica in 150 ml demi-water. The suspension was stirred for 4 h. Subsequently, the catalyst was treated as catalyst PS. The catalyst thus obtained will be denoted as catalyst PSS.

2.2. Flow studies

Activity measurements were performed in a fixed-bed microflow reactor. We verified that the contribution of the homogeneous gas phase reaction was negligible under the chosen conditions: both above and below the catalyst bed about 80 mg of silica (Aerosil 200, Degussa) of a sieve fraction of 500 to 800 micron were mounted. Changing the amount of inert material below the catalyst bed did not affect the conversion, indicating that the reaction was not governed by gas phase radicals reactions. Calculations, moreover, showed that the limitation of transport of mass was negligible under the presently employed conditions [36]. The conversion and the selectivity were measured at atmospheric pressure in a fully automated continuous microflow apparatus. A sieve fraction of catalyst PSS between 150 and 425 micron was placed into a quartz reactor of an internal diameter of 4.5 mm. Reduction of the calcined catalyst was performed in a flow of 10 vol% hydrogen (99.999%) in argon (99.999%) at 720 K for 30 min. The reaction feed consisted of 1 vol% methane (99.995%), and 0.5

vol% oxygen (99.999%) in argon. All gases were provided by Hoek Loos B.V., and used without further purification. The total flow rate was 100 ml(STP)/min, and as directed down-stream. To measure the gas temperature, a chromel–alumel thermocouple was situated at the bottom of the catalyst bed. Analysis of the product gases occurred with a mass spectrometer (Balzers QM420) every 5 to 90 s. An empty reactor displayed less than 1% conversion in the temperature range used in the current study.

To assess the reaction orders with respect to methane and oxygen, 40 mg of catalyst PSS was reduced, and, subsequently, stabilized in a gas mixture containing methane, oxygen, carbon dioxide, and water in argon at 700 K. 3 vol% of water vapor and 1 vol% of carbon dioxide (99.995%, Hoek Loos) were added to the gas mixture. A total flow rate of 100 ml(STP)/min was used. The product gases were analyzed with a Perkin Elmer type 8500 gas chromatograph; methane was detected with a flame ionization detector (FID).

To elucidate the primary products of the reaction between oxygen and methane, 13 mg of catalyst PSS was placed into a quartz reactor. Subsequent to reduction, the catalyst was stabilized in a flow containing 1 vol% methane and 0.5 vol% oxygen in argon at a total flow rate of 400 ml/min at 700 K for several hours.

The total flow rate was varied between 200 and 400 ml(STP)/min at constant methane and oxygen partial pressures. Accordingly, the gas hourly space velocity was thus varied between 500,000 and 1,000,000 h^{-1}. The products were analyzed with the mass spectrometer and the gas chromatograph.

To assess the influence of the palladium crystallite size on the reaction pathway, 60 mg of catalyst either PS or PL was reduced as described above. Subsequently, the temperature of the catalyst was adjusted at 720 K. The catalyst was stabilized in a flow containing 0.5 vol% methane and 0.25 vol% oxygen in argon at a total flow rate of 200 ml(STP)/min. Subsequently, the gas hourly space velocity (GHSV) was varied at constant methane and oxygen partial pressures. The GHSV was varied between 75,000 and 150,000 h^{-1}. Space velocities up to 250,000 h^{-1} were employed using 0.33 vol% methane and 0.17 vol% oxygen, to ensure isothermicity of the reactor.

In one experiment, a gas mixture containing 1 vol% methane and 0.5 vol% oxygen in argon was first combusted over 1 g of an alumina-supported manganese oxide catalyst [37] at 850 K. The thus obtained gas mixture consisted of methane, carbon dioxide, and water vapor in argon.

3. Results and discussion

Figure 1 shows the gas temperature at four different positions in the catalyst bed under reaction conditions, employing PS as a catalyst. With the use of undiluted reactant mixtures, a temperature peak is followed by a temperature drop in the catalyst bed. The temperature profile thus observed agrees nicely with the results of Heitnes et al. [22] for a monolith-supported palladium catalyst. It reflects the initial occurrence of highly exothermic oxidation reactions followed by endother-

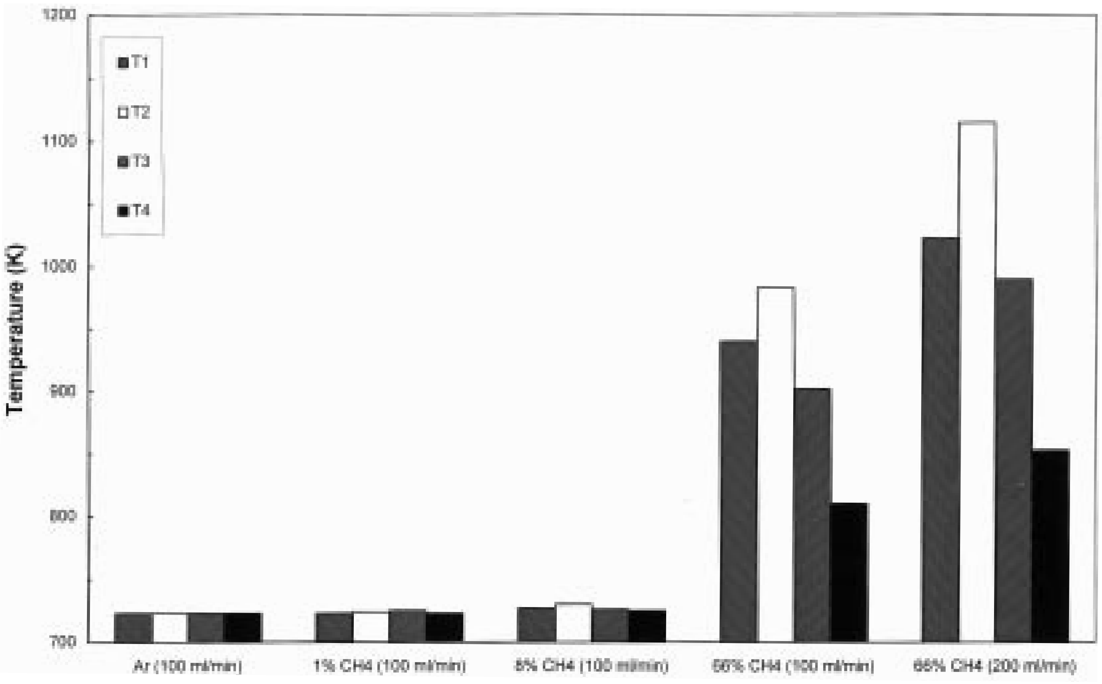

Figure 1. The influence of the composition of the reactant mixture on the temperature profile in the catalyst bed. The height of the catalyst bed was 8 mm. Thermocouples T1, T2, T3, and T4 were placed at about 1, 2, 4, and 7 mm below the uppermost catalyst layer.

mic reforming of methane. The contribution of the direct oxidation of methane to CO and H_2 can, however, not be entirely excluded based on the steep temperature profile only. Therefore, in the present study we investigated the reaction pathway of the palladium-catalyzed partial oxidation of methane in more detail.

With undiluted reactant mixtures, the gas temperatures increases at increasing space velocity, figure 1. In addition, the temperature of the working catalyst surface is probably even higher than the measured gas temperatures [16,19]. As has been extensively discussed [16,17,19] the huge production of thermal energy in the catalyst bed can easily result in erroneous conclusions regarding the reaction pathway. Hence, we conducted our experiments under strictly isothermal conditions by employing diluted reactant mixtures. Figure 1 confirms the excellent isothermicity of the catalyst bed under the conditions applied in the current study, employing a mixture of 1 vol% methane and 0.5 vol% oxygen in argon.

The activity of a previously reduced catalyst PSS was measured as a function of the gas temperature in the catalyst bed. Figure 2 shows that carbon dioxide and water are the products detected at oxygen conversion levels below 100%, while the production of carbon monoxide and hydrogen is observed at temperatures above about 675 K. Qualitatively the same trend was found with catalyst PS and PL. Oscillations are often observed at temperatures around 700 K, figure 2.

To assess the primary reaction products of the partial oxidation of methane to synthesis gas over catalyst PSS, we reduced the contact time to about 4×10^{-3} s to achieve low methane conversion levels, viz. about 4%. Carbon dioxide and water were the only detected products, although – as can be deduced from figure 2 – the temperature was sufficiently high for the production of synthesis gas, viz. 700 K. The essentially zero selectivity to CO and H_2 at low methane conversion level where oxygen is not fully consumed shows that the partial oxidation of methane to synthesis gas starts off with the combustion of methane to carbon dioxide and water. The essentially zero selectivity to CO thus found is in excellent agreement with the observations of König et al. [38], who studied the oxidation of methane under methane-rich conditions over a Pd-film at 773 K for automobile exhaust applications. These authors reported that the CO concentration was unexpectedly low, viz. too low to be measured (< 5 ppm), at CO_2 concentrations of about 4500 ppm under steady-state conditions at low methane conversion levels, viz. about 10%.

The selectivity of recombination reactions on a surface is controlled by the composition of the adsorbed layer. The concentrations of adsorbed species may vary with the reactivity of the catalytic surface, and so does the selectivity. Since the predominant reaction pathway is intimately related to the surface coverage of the reacting species we determined the reaction orders with respect to oxygen and methane. The reaction orders were carefully determined using catalyst PSS under differential conditions: the conversion of methane was kept below about 5%, while both water and carbon dioxide were injected into the reactant stream. Again, carbon

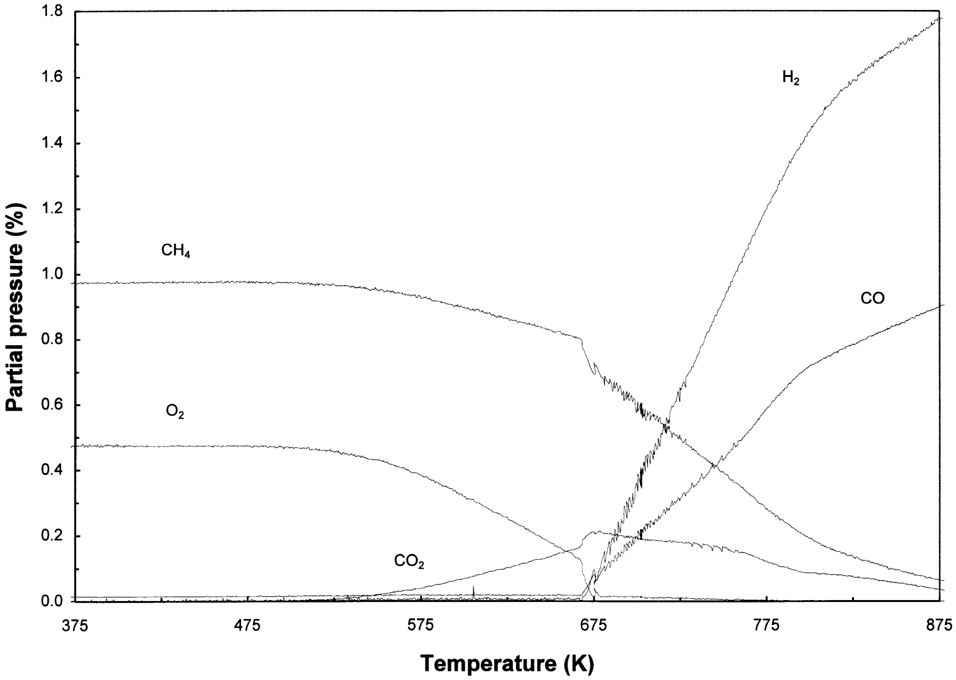

Figure 2. The composition of the product gas as a function of the temperature during the partial oxidation of methane to synthesis gas over catalyst PSS. Oscillations occur in the temperature range from about 675 to 760 K. The reaction products are indicated in the figure.

dioxide and water were the only detected products, although the temperature was sufficiently high for the production of synthesis gas, viz. 700 K. The orders with respect to methane and oxygen are 1.0 and 0.2, respectively, figure 3. These reaction orders indicate that oxygen covers the palladium surface almost completely, whereas methane incidentally contacts the surface, which agrees nicely with the observation that carbon dioxide and water are the solely observed products at low methane conversion levels.

Ostermaier et al. [39] showed that a secondary crystallite size effect such as the reoxidation of the metal surface can be important in oxidation reactions. Since the reaction mechanism, and, hence, the products formed, is closely related to the nature of the active site we briefly compared two equally loaded palladium catalysts of clearly distinct palladium crystallite size. Again, the selectivity to carbon monoxide rapidly dropped at decreasing methane conversion levels, irrespective of the palladium crystallite size, figures 4a and 4b. The selectivity to hydrogen displayed the same trend. Carbon dioxide and water were the only detected products at space velocities sufficiently high to suppress the formation of carbon monoxide and hydrogen. Similar results were obtained at 720 and 970 K. These results confirm that the partial oxidation of methane to synthesis gas starts off with the complete oxidation of methane, irrespective of the palladium particle size.

We investigated, moreover, the propensity of palladium to catalyze the reforming of methane with water vapor and carbon dioxide. To that end, we converted the diluted oxygen/methane reactant mixture into carbon dioxide and water vapor over an alumina-supported manganese oxide catalyst [37] prior to feeding the gas stream to the palladium catalyst. Figure 5 demonstrates that the previous combustion of part of the methane does not affect the overall conversion. Since thermodynamic equilibrium is not achieved this result confirms that carbon monoxide and hydrogen are the products of the sequential combustion and reforming of methane under the employed conditions. The water–gas shift reaction, subsequently, determines the hydrogen to carbon monoxide ratio in the product gas. Hence, the reaction pathway observed with the palladium-catalyzed partial oxidation of methane to synthesis gas closely resembles that of the nickel-catalyzed reaction [11,17–19]. In accordance with the proposed indirect reaction pathway, the use of undiluted reactant mixtures brings about a high temperature peak at the inlet of the catalyst bed, followed by a temperature drop at increasing axial position, figure 1. We conclude that an adiabatic temperature rise of about 1900 K must be taken into account with the partial oxidation of methane to synthesis gas over palladium.

Under the methane-rich conditions employed, the deposition of carbon occurs. Especially, the growth of carbon filaments must be prevented, since these bring about plugging of the reactor [31,40]. Therefore, we investigated the deposition of carbon on the palladium catalyst. The previously reduced catalyst PL was stabilized under reaction conditions at 720 K for 24 h. Subsequently, the top of the catalyst bed was black,

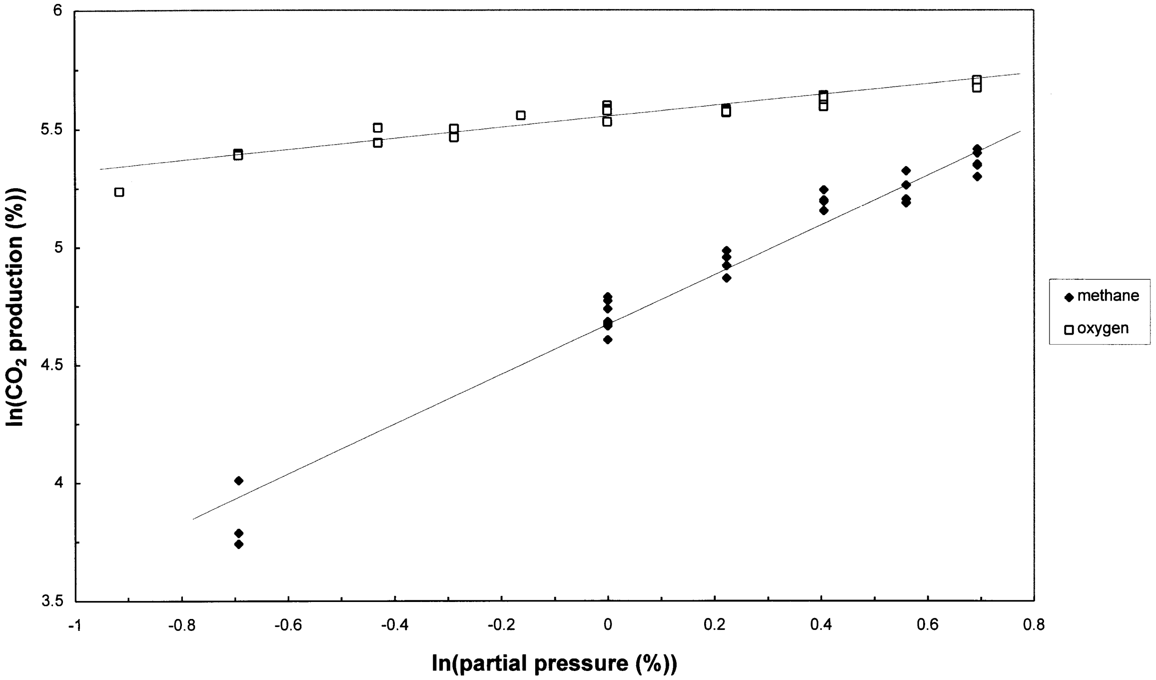

Figure 3. The dependence of the rate of combustion of methane as a function of the partial pressures of methane and oxygen at 700 K, employing PSS as a catalyst.

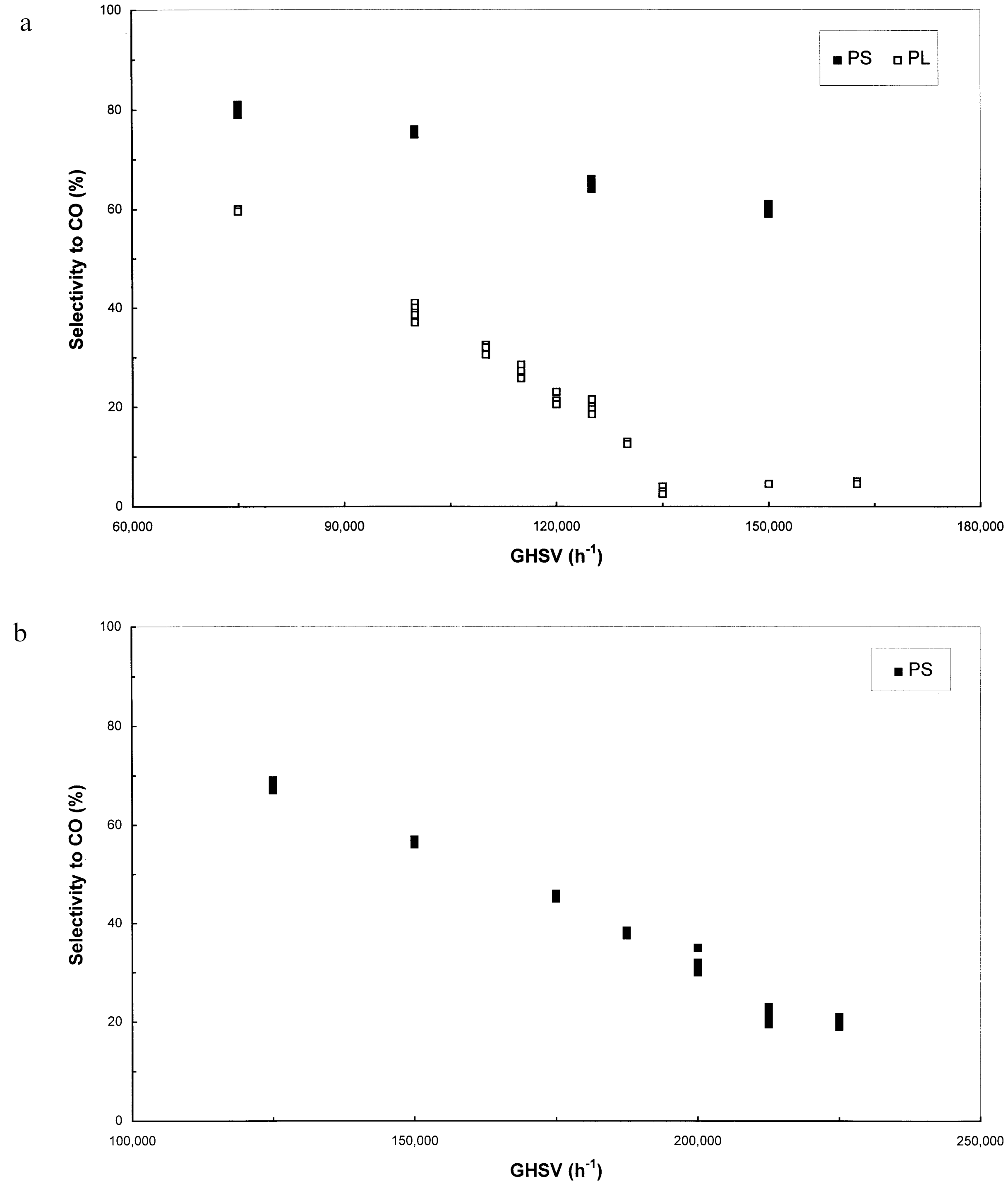

Figure 4. (a) The selectivity to carbon monoxide as a function of the space velocity at 850 K for catalysts of clearly distinct palladium dispersion, viz. catalyst PS and PL. The reactant mixture consisted of 0.5 vol% methane and 0.25 vol% oxygen in argon. Similar results were obtained at 720 and 970 K. (b) The selectivity to carbon monoxide as a function of the space velocity at 850 K, employing PS as a catalyst. The reactant mixture consisted of 0.33 vol% methane and 0.17 vol% oxygen in argon.

whereas the remaining part was grey. Figure 6 represents the X-ray diffraction (XRD) patterns of the upper four of six successive fractions from the catalyst bed. Fraction 1 mainly represents the black top of the catalyst bed. As can be seen, the composition of the catalyst bed in terms of the palladium phase is not uniform along the catalyst bed: only the upper fractions contained palladium carbide [41], showing up along with metallic palladium. Fractions 4, 5, and 6 displayed a similar XRD pattern. Separately conducted in situ ellipsometry measurements showed the presence of metallic and oxidized palladium. Analogously to the

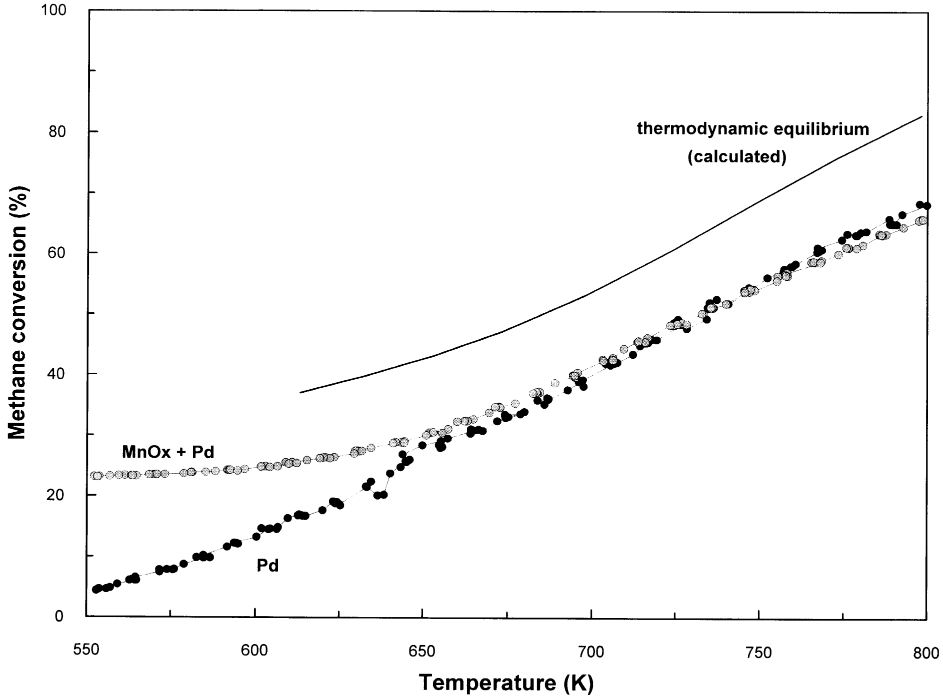

Figure 5. A comparison of the activity of catalyst PS for either the partial oxidation of methane (curve indicated by "Pd") or the reforming of methane with carbon dioxide and water (curve indicated by "MnO_x + Pd"). The reforming mixture was prepared by the previous combustion of the methane/oxygen reactant mixture over a manganese oxide catalyst.

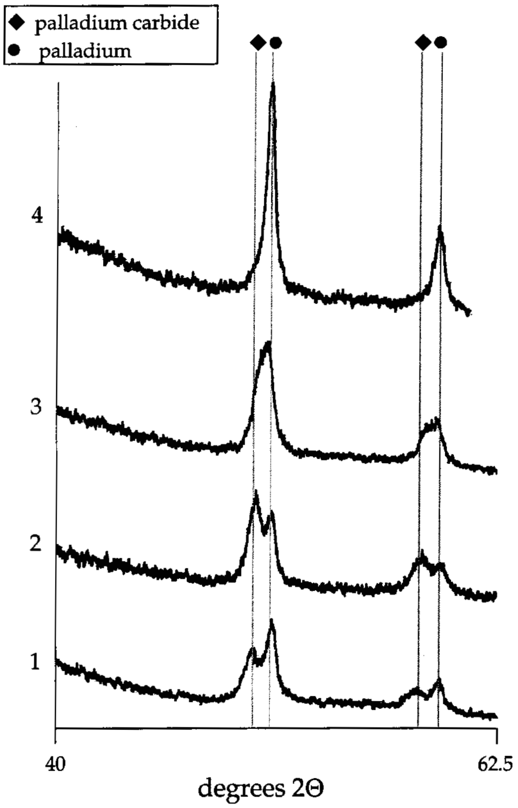

Figure 6. X-ray diffraction patterns of four successive fractions from the catalyst bed subsequent to stabilization of catalyst PL during reaction at 720 K for 24 h. The vertical lines serve only to guide the eye.

nickel-catalyzed reaction [30], the simultaneous presence of oxidic, carbidic, and metallic palladium should be borne in mind when investigating the partial oxidation of methane to synthesis gas. The non-uniform phase composition along the catalyst bed renders the use of pulse experiments to elucidate the mechanism dangerous.

Transmission electron microscopy (TEM), moreover, revealed that mainly catalyst fractions 2 and 3 had grown filamentary carbon, figure 7. Close examination of the electron micrographs revealed that the large crystallites, viz. 15 to 20 nm, predominantly contribute to the growth of carbon filaments. Hence, in addition to heat management problems owing to the steep temperature profile, plugging of the reactor owing to the growth of carbon filaments must be taken into account under the employed conditions.

4. Conclusions

(1) The palladium-catalyzed partial oxidation of methane to synthesis gas involves the sequential combustion and reforming of methane. Hence, an adiabatic temperature rise of about 1900 K must be taken into account with the partial oxidation of methane to synthesis gas over palladium.

(2) The composition of the palladium phase is not uniform along the catalyst bed. Hence, the results of

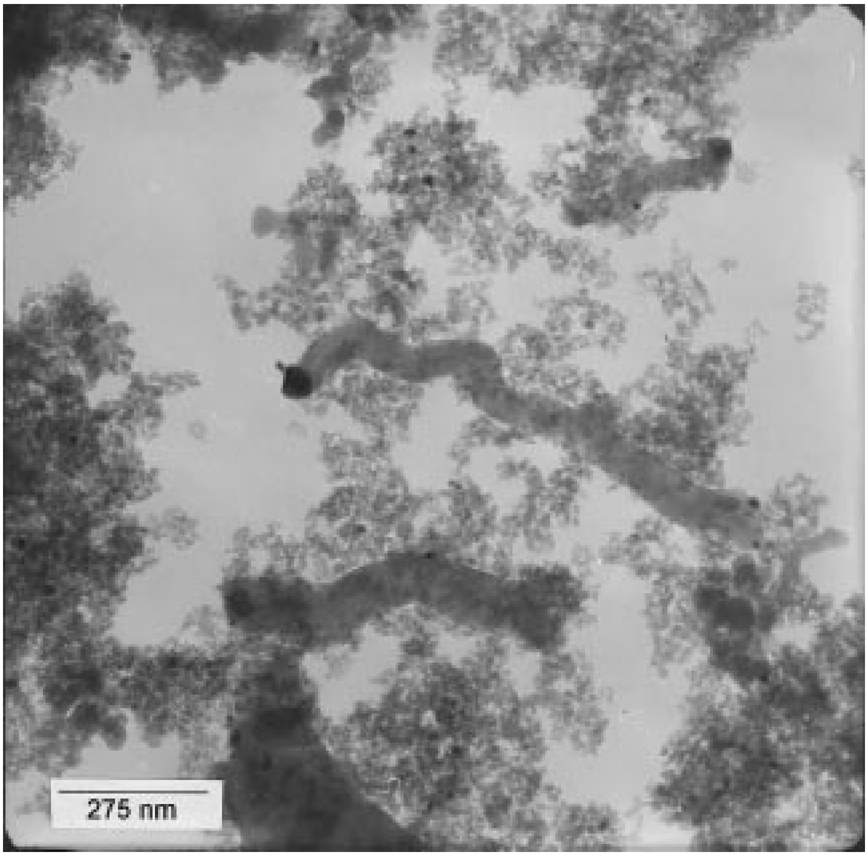

Figure 7. Transmission electron micrograph of fraction 2 from the catalyst bed subsequent to stabilization of catalyst PL during reaction at 720 K for 24 h.

mechanistic studies using a pulse apparatus should be considered with care.

(3) Carbon filaments grow from large palladium crystallites, viz. 15 to 20 nm, under the methane rich conditions employed.

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