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Isotopic Transient Kinetic Analysis of the Induction Phenomenon for Methanol Synthesis on Pd/SiO_2

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Steady-state isotopic transient kinetic analysis (SSITKA) was used to study the induction phenomenon observed for the rate of methanol (MeOH) synthesis on Pd/SiO_2 by evaluating the surface concentration of the active intermediates leading to MeOH (N_{MeOH}) and their residence times (τ_{MeOH}) for the beginning and for the end of the induction period. The existence of the induction effect was found to be unaffected by the partial pressure of CO and/or H_2; however, its magnitude (i.e., the ratio of the maximum rate of formation of MeOH to the initial rate) was higher for lower H_2/CO ratios where the catalyst had lower initial activities for MeOH synthesis. By accounting for the effect of interparticle readsorption of MeOH on the surface reaction parameters obtained by SSITKA (N_{MeOH} and τ_{MeOH}), it was found that, during the induction period, the surface concentration of the active intermediates leading to MeOH (N_{MeOH}) increased significantly while the pseudo-first-order intrinsic activity of the sites leading to MeOH ($1/\tau_{MeOH}$) remained constant. Thus, the induction period for MeOH synthesis over Pd/SiO_2 can best be attributed to an increase in the number of active sites/intermediates forming MeOH. The possible modifications of the Pd which might cause the induction effect are discussed in detail.

INTRODUCTION

Pd has been found to be one of the best catalysts for the synthesis of methanol (MeOH) because of its weak ability to dissociate CO and its moderate ability to activate H_2 (1–3). A large number of studies [including (4–7)] have focused on determining the activity, selectivity, and mechanism of this reaction on supported Pd catalysts. Other studies have addressed the impact of promoters, supports, and methods of preparation (8–11). However, no study has focused on the cause of the induction period, seen often in MeOH synthesis over supported Pd catalysts.

The induction phenomenon in the rate of synthesis of MeOH on supported Pd catalysts has been found in another study in this laboratory to occur no matter the Pd precursor or support used (12). However, the length of the induction period and the magnitude of the induction phenomenon are dependent on the type of the Pd precursor and the nature of the support. It appears that this induction phenomenon for MeOH synthesis is not only common for supported Pd catalysts but also for quite a wide variety of other catalysts, such as Ru/Al_2O_3 (13), $CeCu_2$ (14), and Cu/ZnO (15).

Due to the simplicity of the Pd/SiO_2 catalytic system and because of its high activity and selectivity toward MeOH formation without the presence secondary reactions [such as the formation of dimethyl ether (DME) from the MeOH formed], it was chosen for studying the induction phenomenon using both standard reaction and steady-state isotopic transient kinetic analysis (SSITKA) techniques. SSITKA is perhaps the most powerful kinetic technique for characterizing surface reaction parameters under reaction conditions. It permits one to determine surface concentrations of active intermediates and their surface residence times. SSITKA and its application have recently been reviewed in detail (16).

EXPERIMENTAL

Materials

The surface area and the pore volume of the SiO_2 support used (Davison 952), obtained by nitrogen physisorption at 77 K, were found to be 219 m^2/g and 0.51 cm^3/g, respectively. The impurities in the SiO_2 were determined by inductively coupled plasma (ICP) to be Mg (150 ppm), Na (570 ppm), Ca (750 ppm), Ti (120 ppm), Al (220 ppm), Fe (96 ppm), P (83 ppm), K (160 ppm), and S (30 ppm). Palladium chloride (Aldrich) was used for preparing the Pd catalyst.

Catalyst Preparation

A 5 wt% Pd/SiO_2 catalyst was prepared by the incipient wetness technique using an aqueous solution of $PdCl_2$. After the impregnation step, the catalyst was dried in an oven for 12 h at 115°C. The dried catalyst was then calcined in flowing air (Praxair, 99.999% pure) by raising the catalyst temperature to 400°C with a heating rate of 1°C/min and holding for 5 h. After that, the catalyst was reduced in flowing H_2 (Praxair, 99.999% pure) at 400°C for 5 h following a

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1°C/min ramp. Finally, the reduced catalyst was passivated in a stream of 2% O_2 in He (Praxair, 99.999% pure) at room temperature for 2 h.

Elemental Analysis

ICP (Galbraith Laboratories, Inc.) was used to determine the loading of Pd for the prepared Pd/SiO_2 catalyst. The loading of Pd found to be 5 wt% of Pd (12) as expected due to the method of preparation used.

CO Chemisorption

CO chemisorption measurements were carried out according to the method used by Kazi *et al.* (17). The catalyst was rereduced with hydrogen (Praxair, 99.999% pure), flowing at a rate of 60 cm^3/min, for 5 h at 400°C following a 1°C/min ramp. Desorption of hydrogen from the catalyst surface was done at 400°C for 1 h to achieve a vacuum less than 10^{-6} mm Hg. CO was then introduced to the cell containing the reduced catalyst at room temperature and allowed to equilibrate with the Pd surface for 15 h. Total adsorption isotherm data were collected at room temperature by the decreasing pressure method. Each sequential datum of the isotherm was obtained after 2 h. The total amount of chemisorbed CO molecules $[CO_{tot}]$ was calculated by extrapolating the total adsorption isotherm to zero pressure. After determination of the total adsorption isotherm, the chemisorption cell was evacuated for 20 min at room temperature, and the reversible adsorption isotherm was measured at room temperature. This isotherm was also extrapolated to zero pressure to obtain CO_{rev}. The number of Pd metal atoms at the surface was determined using the relationship $CO_{irrev}/Pd_s = 1$, where $CO_{irrev} = CO_{tot} - CO_{rev}$. It is important to note that the calculated average particle size of Pd/SiO_2 based on this method is in a very good agreement with values obtained using TEM (17). The average particle size of the Pd crystallites (d_p) was found to be 5.5 nm according to the equation

$$d_p\,(\text{nm}) = \frac{5 * \text{wt. fraction of Pd (g Pd/g cat)} * (10^7\ \text{nm/cm})^3}{CO_{irrev}\ (\text{mol/g cat}) * N_{Avo}\ (\text{atom/mol}) * SA_{Pd}\ (\text{nm}^2/\text{atom}) * \rho_{Pd}\ (\text{g Pd/cm}^3)},$$

while the dispersion of the Pd particles was found to be 17% with a maximum experimental error of ±0.9% (12).

Carbon Monoxide Hydrogenation

A micro, fixed-bed reactor was used for studying this reaction, and differential reaction conditions were employed to minimize mass and heat transfer limitations. A flow of 60 cm^3/min of H_2 (Praxair, 99.999% pure) was used first to rereduce 0.05 g of a catalyst, ramping the temperature by 1°C/min to 400°C and holding for 5 h. After the rereduction was completed, the reaction was started at 220°C and 1.8 atm by setting the total flow of H_2 (Praxair, 99.999% pure), CO (Praxair, 99.999% pure), and He (Praxair, 99.999% pure) to be equal to 36 cm^3/min (STP). The reactants were further purified using a Matheson 450 Purifier filled with 4A molecular sieve (for CO) and an Alltech Gas Purifier packed with Drierite and 5A molecular sieve (for H_2). The flow rate of H_2 was varied between 16 and 32 cm^3/min, while that for CO was varied between 2 and 4 cm^3/min, with He providing the balance. After 3 min reaction, the first sample of the products was taken and analyzed using a Varian 3700 gas chromatograph (GC) equipped with a 6-ft Porapak-Q column and an FID detector. The reaction was followed for 2 h.

Isotopic transient measurements were taken by switching from ^{12}CO to ^{13}CO after 3, 30, 60, and 120 min reaction. A Leybold–Inficon Auditor-2 mass spectrometer (MS) with a high-speed data acquisition system was used to detect the amounts of different isotopically labeled species. Differential pumping to control gas leakage to the MS and minimum process line length were used to reduce the gas phase residence time in the system. A pneumatic electronically operated valve was used to switch between a reactant stream containing normal carbon monoxide (^{12}CO) (Praxair, 99.999% pure) and another stream containing labeled carbon monoxide (^{13}CO) (Isotech, 99.999% pure). The switching between ^{12}CO and ^{13}CO input flows was done without affecting the stability of the reaction. Ar was used as a tracer in the ^{12}CO flow to account for the gas phase holdup. The concentration of Ar (5% of the ^{12}CO stream) was not sufficient to perturb the reaction stationary state during the switch from $^{12}CO + Ar$ to ^{13}CO.

Readsorption effects on the SSITKA parameters were determined after steady-state reaction was established at 220°C and 1.8 atm. The total flow rate of the reactants mixture was varied between 18 and 45 cm^3/min for a partial pressure of CO of 0.2 atm and partial pressures of H_2 of 1.6 and 0.8 atm.

Stop-flow measurements were used to determine the amount of carbon deposited on the surface of the Pd/SiO_2 catalyst. Selected reaction conditions (220°C, $P_{CO} = 0.2$ atm, and $P_{H_2} = 0.8$ or 1.6 atm) were used in performing these experiments. The amounts of carbon deposited after 3, 30, and 120 min reaction were determined. This was done by shutting off the reactant stream containing CO, H_2, and He at the specified time, flushing the reactor for 5 min with He, then flowing H_2 and He ($P_{H_2} = 0.8$ or 1.6 atm) for 10 min and monitoring the effluent gas stream by MS. The amount of surface carbon was determined by integrating the curve for the rate of CH_4 formed with time. No MeOH desorption was detected during this stop-flow procedure. After 10 min reaction at 220°C, the temperature was ramped to 400°C without any additional CH_4 formation being detected for any of the runs.

RESULTS

Table 1 contains the results of CO hydrogenation on Pd/SiO_2 at 220°C and 1.8 atm at 3 and 30 min reaction, corresponding to the initial and maximum (end of induction period) values of CO conversion to MeOH, respectively. The highest CO conversion under the conditions used was less than 1%, meaning that differential reaction conditions could be assumed. No evidence of mass or heat transfer limitations was detected for any of the reaction experiments as evidenced by appropriate apparent activation energies for the formation of MeOH. The apparent activation energy of MeOH formation at steady state was equal to 62 kJ/mol, similar to values reported in the literature for supported Pd catalysts (6, 7). The conversions of CO to MeOH for the various conditions studied were much smaller than those for equilibrium (less than 10% of the equilibrium conversion). Thus, based on this fact and the appropriateness of the apparent activation energy of MeOH, it can be concluded that MeOH synthesis was limited kinetically and not thermodynamically. The H_2/CO ratios used were high enough, ranging between 4 and 16, to minimize deactivation at steady state. The selectivity for MeOH formation was 99% at all times except during the initial period where it was in the range of 87–96% depending on conditions.

The rate of formation of MeOH and TOF_{CO} (TOF based on irreversible chemisorbed CO) increased with increasing P_{H_2} and/or P_{CO} for the ranges of partial pressures of H_2 and CO studied as shown in Table 1 (note that %CO converted did not always increase with increasing P_{CO} at constant P_{H_2} due to an increase in CO flow rate). The rate of formation of MeOH is a direct function of both P_{H_2} and P_{CO} (Figs. 1 and 2). The same relationship appeared to hold throughout the time-on-stream of CO hydrogenation reaction. By plotting the rate of formation of MeOH at steady state versus P_{H_2} holding P_{CO} constant (Fig. 3), versus P_{CO} holding P_{H_2} constant (Fig. 4), and versus P_{MeOH} holding P_{H_2} and P_{CO} constant (Fig. 5), the exponents for the partial pressures of H_2, CO, and MeOH in the power law rate expression for MeOH formation (at low CO conversion) were determined. This expression is given by

$$\mathrm{Rate}_{\mathrm{MeOH}} = kP^{a}_{\mathrm{H_2}}P^{b}_{\mathrm{CO}}P^{c}_{\mathrm{MeOH}},$$

where the exponents for P_{H_2} and P_{CO} are approximate since P_{MeOH} was not held constant in their determination.

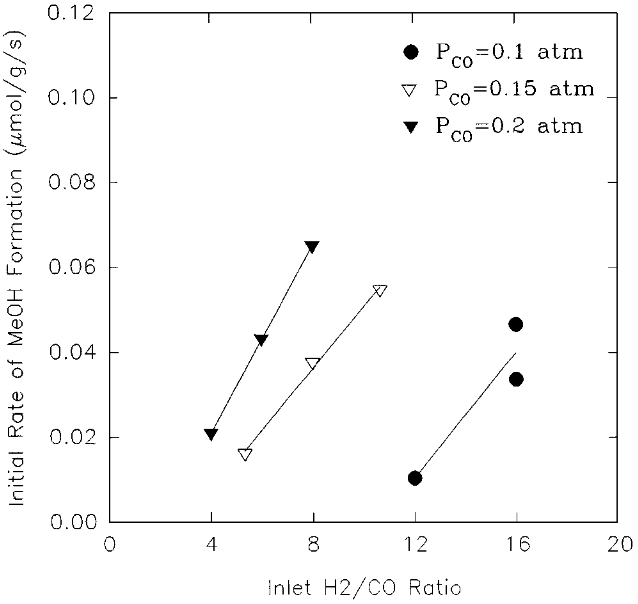

FIG. 1. Initial rate of formation of MeOH vs H_2/CO ratio (at 220°C).

TABLE 1

CO Hydrogenation Results at 220°C for Pd/SiO_2

		CO conversion (%)		MeOH selectivity (%)		Rate of formation of MeOH (μmol/g/s)		TOF_{CO}[a] (10^{-3} s^{-1})	
P_{H_2} (atm)	P_{CO} (atm)	Init.[b]	Max.[c]	Init.[b]	Max.[c]	Init.[b]	Max.[c]	Init.[b]	Max.[c]
0.8	0.10	0.04	0.08	87	98	0.01	0.02	0.1	0.3
0.8	0.15	0.05	0.08	87	98	0.02	0.03	0.3	0.4
0.8	0.20	0.04	0.07	89	98	0.02	0.04	0.3	0.5
1.2	0.10	0.13	0.22	92	98	0.03	0.06	0.4	0.8
1.2	0.15	0.09	0.15	96	98	0.04	0.06	0.5	0.8
1.2	0.20	0.08	0.12	94	98	0.04	0.06	0.6	0.8
1.6	0.10	0.17	0.28	96	98	0.05	0.07	0.6	0.9
1.6	0.15	0.14	0.19	96	98	0.05	0.08	0.7	1.0
1.6	0.20	0.12	0.15	96	98	0.06	0.08	0.8	1.0

[a] Based on CO_{irrev} chemisorption.
[b] After 3 min reaction.
[c] After 30 min reaction.

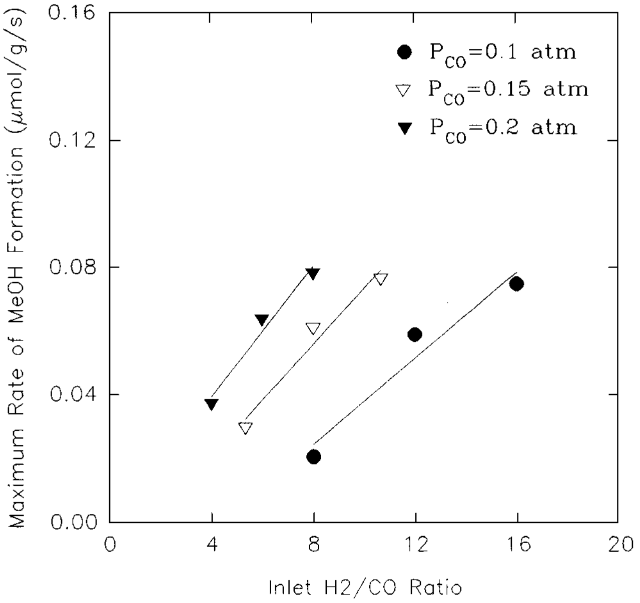

FIG. 2. Maximum rate of formation of MeOH vs H_2/CO ratio (at 220°C).

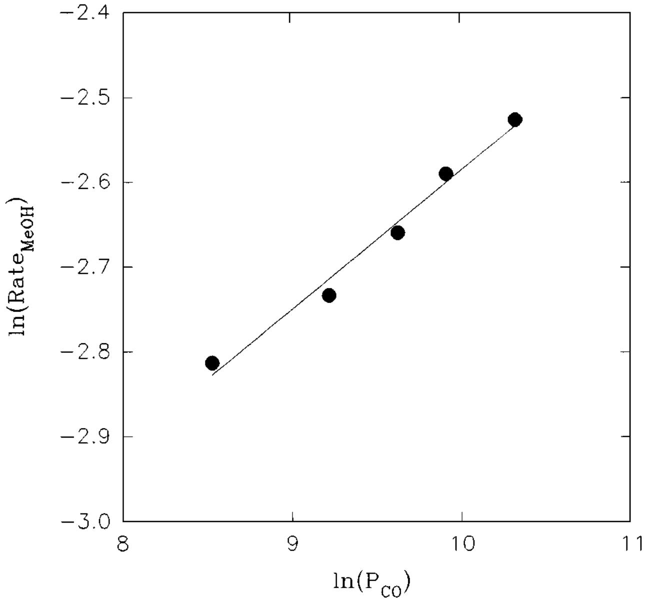

FIG. 4. Steady-state rate of formation of MeOH vs P_{CO} (in Pascals) (at $P_{\mathrm{H_2}} = 1.6$ atm and 220°C).

However, due to the small dependence of rate on P_{MeOH} ($c = -0.15$) the exponents can be considered reasonably accurate. The exponent determined for $P_{\mathrm{H_2}}$ (a) was found to range between 1.16 and 1.8 as the value of P_{CO} held constant varied from 0.2 to 0.1 atm, respectively. The exponent for P_{CO} (b) ranged from 0.16–1.0 for $P_{\mathrm{H_2}}$ held constant between 1.6 and 0.8 atm, respectively. The partial pressure of MeOH was varied by varying the flow rate at constant H_2 and CO partial pressure. This introduces some uncertainty as to the exact value for the exponent. However, this uncertainty is more than compensated for by the fact that the value represents the impact of MeOH at very low partial pressures, as are typically present during differential reaction.

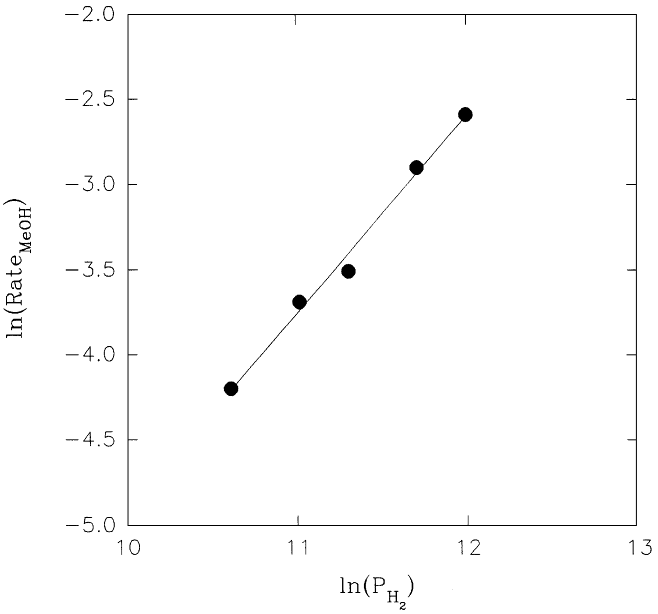

FIG. 3. Steady-state rate of formation of MeOH vs $P_{\mathrm{H_2}}$ (in Pascals) (at $P_{\mathrm{CO}} = 0.2$ atm and 220°C).

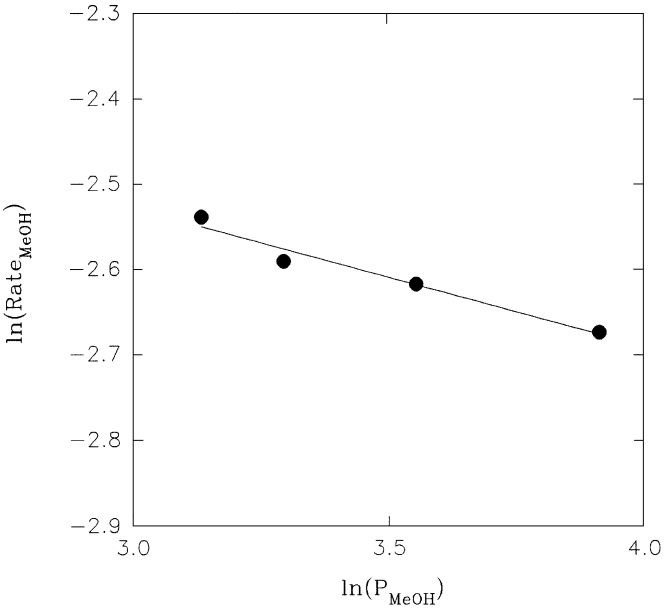

FIG. 5. Steady-state rate of formation of MeOH vs P_{MeOH} (in Pascals) (at 1.8 atm and 220°C).

The time-on-stream behavior of the rate of formation of MeOH (Fig. 6) indicates that the reaction behaviors at various P_{H_2} and P_{CO} were the same qualitatively but not quantitatively, with an induction period in the rate of formation of MeOH occurring for all the reaction conditions used. The time of the induction period was ≤30 min for all the different reaction conditions. Figure 7 shows that the induction factor (the ratio between the maximum and the initial rate of formation of MeOH) was more significant for conditions where the initial catalyst activity was lower (lower H_2/CO ratios).

SSITKA was used to determine the surface concentration of active MeOH intermediates and their average residence times. Figure 8 shows a typical set of normalized isotopic transients for MeOH ($^{12}CH_3OH$) and Ar obtained by switching between a stream containing ^{12}CO and Ar and another stream containing ^{13}CO after 30 min of reaction at 220°C and for partial pressures of H_2 and CO of 1.6 and 0.2 atm, respectively. Methane and CO transients could not be followed at the same time as those for MeOH due to the methane concentration being below the detectibility limit of the MS and CO detection requiring an incompatible setting (compared to MeOH) for the MS. The average surface residence time for the intermediates leading to MeOH (τ_{MeOH}) is equal to the area between the normalized transients of MeOH and Ar. Table 2 shows the results for τ_{MeOH} at the beginning and the end of the induction period for different values of P_{H_2} and P_{CO}. It can be seen that P_{H_2} had a significant impact on the value of τ_{MeOH}, while P_{CO} had little if any effect. τ_{MeOH} decreased with increasing P_{H_2}.

By multiplying the calculated value for τ_{MeOH} by the rate of formation of MeOH, the surface abundances of the

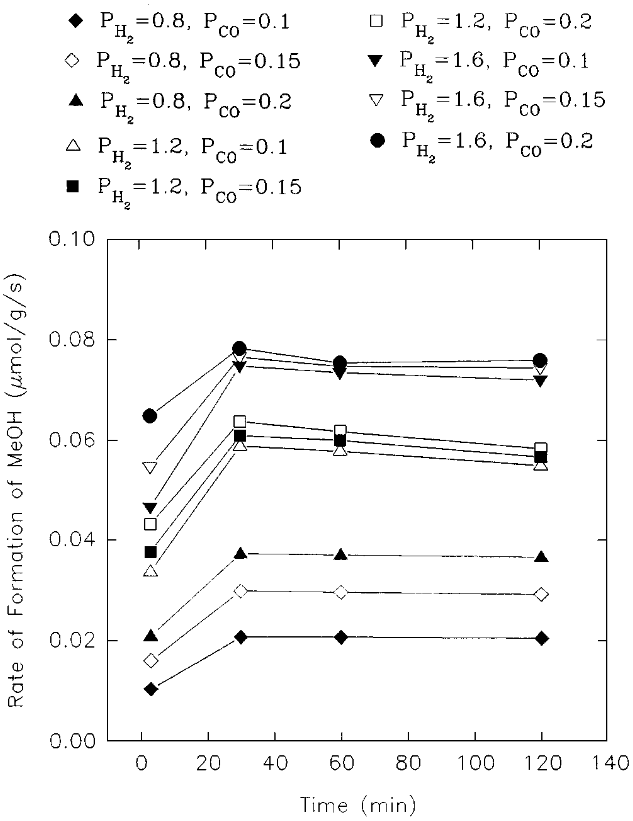

FIG. 6. Rate of formation of MeOH vs time-on-stream during CO hydrogenation at different partial pressures of H_2 and CO (at 220°C and 1.8 atm).

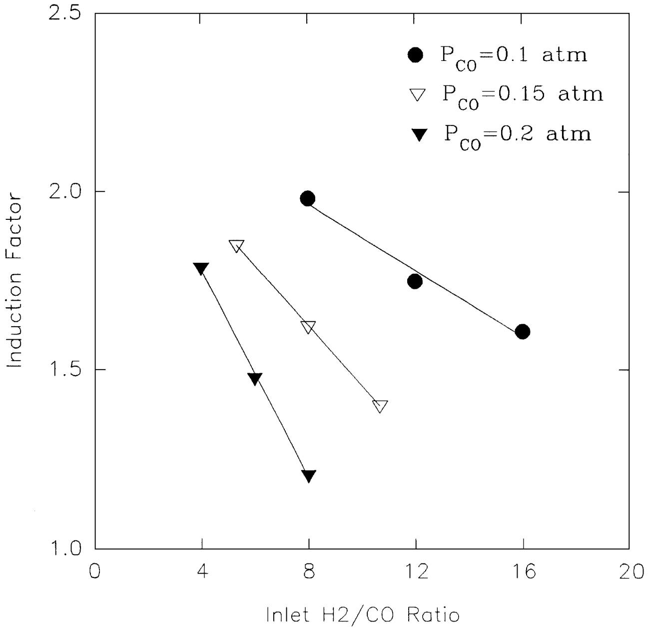

FIG. 7. Induction factor vs H_2/CO ratio (at 220°C).

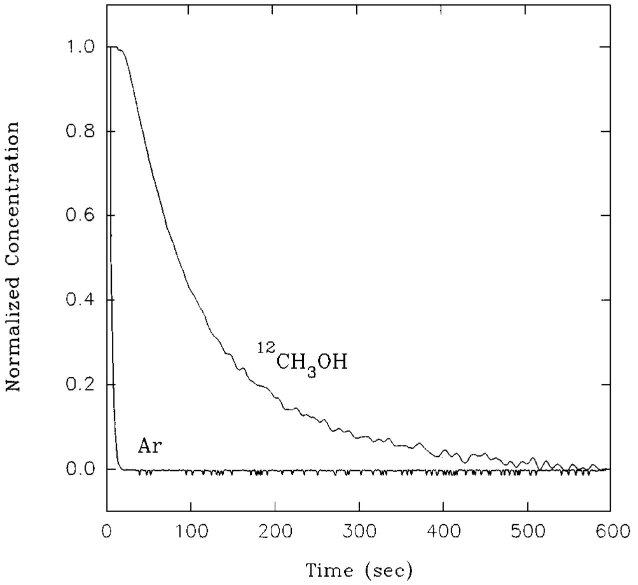

FIG. 8. Typical transients of $^{12}CH_3OH$ and Ar vs time.

TABLE 2

SSITKA Results for MeOH Synthesis at 220°C on Pd/SiO$_2$

		Rate of formation of CH$_3$OH (μmol/g/s)		τ_{MeOH} (s)		N_{MeOH} (μmol/g)		Θ_{MeOH}[a]	
$P_{\mathrm{H_2}}$ (atm)	P_{CO} (atm)	Init.[b]	Max.[c]	Init.[b]	Max.[c]	Init.[b]	Max.[c]	Init.[b]	Max.[c]
0.8	0.10	0.01	0.02	148	151	1.5	3.1	0.02	0.04
0.8	0.15	0.02	0.03	150	151	2.6	4.6	0.03	0.06
0.8	0.20	0.02	0.04	150	151	3.1	5.7	0.04	0.07
1.2	0.10	0.03	0.06	136	135	4.6	8.0	0.06	0.10
1.2	0.15	0.04	0.06	133	132	4.8	8.0	0.06	0.10
1.2	0.20	0.04	0.06	132	132	5.6	8.5	0.07	0.11
1.6	0.10	0.05	0.07	126	122	5.7	9.0	0.07	0.11
1.6	0.15	0.05	0.08	124	122	6.7	9.4	0.08	0.12
1.6	0.20	0.06	0.08	126	121	8.1	9.5	0.10	0.12

[a] Based on CO$_{\mathrm{irrev}}$ chemisorption.

[b] After 3 min reaction.

[c] After 30 min reaction.

intermediates leading to MeOH (N_{MeOH}) were determined. Table 2 shows that N_{MeOH} increased with either increasing $P_{\mathrm{H_2}}$ or increasing P_{CO} in the range used in this investigation. Hence, the coverage of intermediates leading to MeOH (Θ_{MeOH}) had its maximum value at the highest H$_2$ and CO partial pressures, 1.6 and 0.2 atm, respectively.

DISCUSSION

There are two main issues being addressed by this paper: (a) the change in the surface reaction parameters during the induction period for the synthesis of MeOH on supported Pd catalysts, and (b) how reaction conditions affect this induction phenomenon. SSITKA can provide important insight into these issues; however, one has to be careful in the interpretation of the SSITKA results due to the readsorption of MeOH. To accurately interpret the SSITKA measurements, the impact of the readsorption of MeOH on the parameters obtained by SSITKA has to be delineated (18).

By performing CO hydrogenation at different flow rates, the impact of interparticle readsorption on the parameters obtained by SSITKA was able to be identified. By plotting both τ_{MeOH} and N_{MeOH} versus space time, the average residence time of the reactant mixture in the porous catalyst bed (Figs. 9 and 10), it is clear that both τ_{MeOH} and N_{MeOH} increased with increasing space time, regardless of $P_{\mathrm{H_2}}$. The increase in the values of both τ_{MeOH} and N_{MeOH} with increasing space time is due to increased readsorption of MeOH on active, less active, and/or inactive sites in/on other catalyst particles (granules). Figure 9 shows that τ_{MeOH} was increased by as much as 25% upon the doubling of the space time, while Fig. 10 shows that N_{MeOH} increased by as much as 20%. These results show clearly that interparticle readsorption contributes significantly to the values of the parameters obtained by SSITKA for MeOH synthesis (τ_{MeOH} and N_{MeOH}) over Pd/SiO$_2$, as also previously found by Vada and Goodwin (18). Figure 9 also shows that upon increasing $P_{\mathrm{H_2}}$, τ_{MeOH} decreased. This is due to the fact that $1/\tau_{\mathrm{MeOH}} = k_{\mathrm{R}}\ [N_{\mathrm{H}}]$ for MeOH synthesis under these conditions, where N_{H} is the surface concentration of adsorbed hydrogen. In other words, due to the dependency of τ_{MeOH} on N_{H}, the increase in N_{H} brought about by the increase in $P_{\mathrm{H_2}}$ resulted in a decrease in τ_{MeOH}. Figure 10 shows that upon increasing $P_{\mathrm{H_2}}$, N_{MeOH} also increased. The determination of N_{MeOH} is based on a simple mass balance and does not include any direct dependence on N_{H}. However, its increase can be suggested to be due to an enhanced hydrogenation of surface CO brought about by the increase

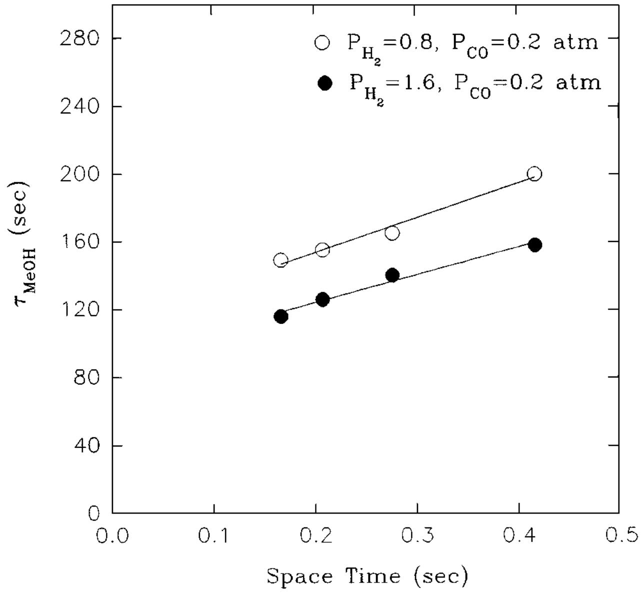

FIG. 9. τ_{MeOH} vs space time (at 220°C, 1.8 atm, and steady-state).

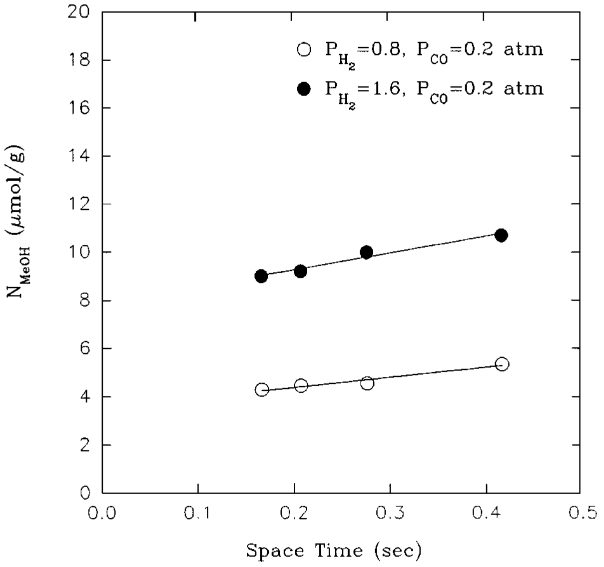

FIG. 10. N_{MeOH} vs space time (at 220°C, 1.8 atm, and steady-state).

in hydrogen surface coverage with increasing P_{H_2}. As can clearly be seen in Fig. 10, P_{H_2} had a much greater effect on N_{MeOH} than P_{MeOH} (a direct function of space time). P_{CO} really only had a significant effect on N_{MeOH} at the lowest partial pressure of H_2 (see Table 2).

The slopes of the lines in Fig. 9 for two different reaction conditions (at the two most different partial pressures of H_2) are almost constant and are equal to 180 ± 20. By extrapolating the values of τ_{MeOH} to space time = 0 (which corresponds to infinite flow through the catalyst bed), a more accurate estimate of MeOH surface residence time due to reaction (τ^0_{MeOH}) which minimizes the effect of readsorption can be determined. Note that this procedure does not eliminate readsorption effects within the pores of the primary catalyst particle (granule), which are much more difficult to remove. Making the assumption that the slopes of the lines of τ_{MeOH} versus space time hold approximately constant at 220°C for the conditions used (which appears to be the case), a more exact assessment of the variation in τ_{MeOH} can be made. Table 3 contains the corrected values of τ_{MeOH} (τ^0_{MeOH}) for the various reaction conditions. Table 3 clearly shows that, during the induction period, τ^0_{MeOH} remained almost constant for all partial pressures of H_2 and CO used. The increase in P_{MeOH} with an increase in the rate of formation of MeOH during the induction period would be expected to result in a decrease in the readsorption contribution to the values of τ_{MeOH} for all partial pressures of H_2 and CO used due to the increase in the competition among MeOH molecules for readsorption on the available sites. However, this effect seems to be small relative to the measured values of τ_{MeOH} probably due to the low partial pressures of MeOH. The expected variations in τ_{MeOH} due to the small changes in P_{MeOH} seem to lie within the experimental error of the measured SSITKA parameter (τ_{MeOH}). Hence, for the different operating reaction conditions used in this investigation, the overestimation of τ_{MeOH} due to readsorption during the induction period was mainly affected by the space time rather than by the variation in P_{MeOH}. The pseudo-first-order rate constant, where rate $= k^0 N_{MeOH}$, for this reaction can be estimated by $k^0 = 1/\tau^0_{MeOH}$ (Table 3). Due to the lack of variation in τ^0_{MeOH} during the induction period, k^0 also remained essentially constant.

From Figs. 6 and 11 it is clear that a trend exists between the rate of formation of MeOH and N_{MeOH}. Both the rate of formation of MeOH and N_{MeOH} had low initial values that increased through the induction period until reaching their maximum values after ≤30 min reaction. After that, the rate of formation of MeOH and N_{MeOH} exhibited steady values. As was the case for τ_{MeOH} vs space time, it was found that the data for N_{MeOH} vs space time (Fig. 10) could be fit with straight lines having constant slopes of 5.5 ± 1.5. By correcting the values of N_{MeOH} experimentally obtained for interparticle readsorption, it was possible to more accurately evaluate the impact of the induction phenomenon on the surface abundance of MeOH intermediates (reported in Table 3 as N^0_{MeOH}). For the operating conditions used in this investigation, the maximum increase in N^0_{MeOH} during the induction period was as much as ca. 400% (at a partial pressure of H_2 of 0.8 atm) for a doubling in the rate of formation of MeOH (see Table 3). Thus, there was a significant true increase in the number of surface intermediates of MeOH during the induction period accounting for most of the increase in activity seen.

Some suggestions have been made in the literature that MeOH synthesis may be affected by the particle size of the supported Pd catalysts (19–21). In order to determine whether a change in the dispersion of the Pd was the cause

TABLE 3

Corrected SSITKA Results for MeOH Synthesis at 220°C on Pd/SiO$_2$

P_{H_2} (atm)	P_{CO} (atm)	τ^0_{MeOH} (s) Init.[a]	τ^0_{MeOH} (s) Max.[b]	$k^0 = 1/\tau^0_{MeOH}$ (10^{-3} s^{-1}) Init.[a]	$k^0 = 1/\tau^0_{MeOH}$ (10^{-3} s^{-1}) Max.[b]	N^0_{MeOH} (μmol/g) Init.[a]	N^0_{MeOH} (μmol/g) Max.[b]
0.8	0.10	111	114	9.0	8.8	0.4	1.9
0.8	0.15	113	114	8.8	8.8	1.4	3.4
0.8	0.20	113	114	8.8	8.8	1.9	4.5
1.2	0.10	99	98	10.1	10.2	3.4	6.8
1.2	0.15	96	95	10.4	10.5	3.6	6.8
1.2	0.20	95	95	10.5	10.5	4.4	7.3
1.6	0.10	89	85	11.2	11.8	4.5	7.8
1.6	0.15	87	85	11.5	11.8	5.5	8.2
1.6	0.20	89	85	11.2	11.9	6.9	8.3

[a] After 3 min reaction.
[b] After 30 min reaction.

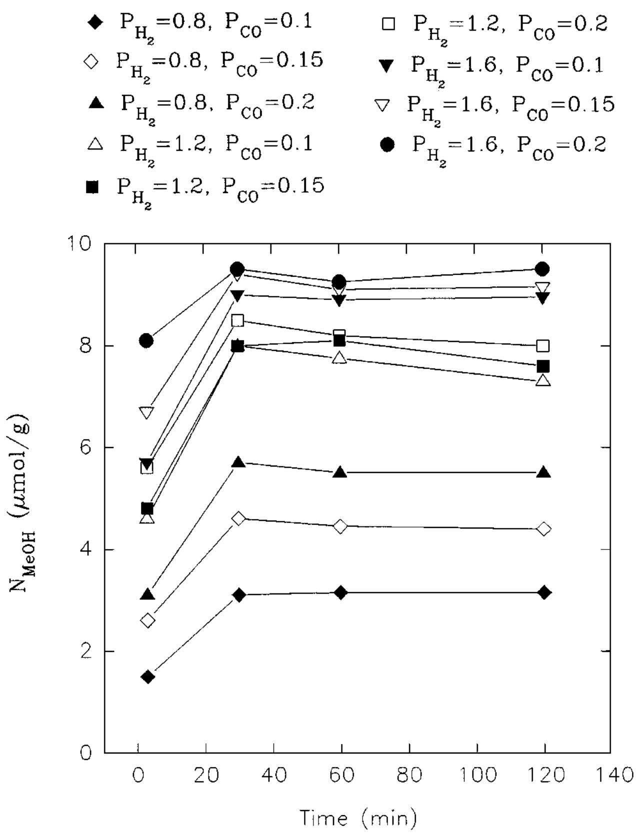

FIG. 11. N_{MeOH} vs time-on-stream for reaction at different partial pressures of H_2 and CO (at 220°C and 1.8 atm).

of the observed induction phenomenon in this study, experiments were carried out to measure the initial reaction characteristics of the used and regenerated catalyst (regenerated by rereducing the used catalyst in a stream of H_2 according to the standard reduction procedure reported under Experimental). It is clear from Fig. 12 that there were no detectible differences between the activity (including the occurrence of the induction period) of the fresh and the used (regenerated) catalyst for MeOH synthesis at various times-on-stream. Thus, the results of MeOH synthesis for the fresh and the regenerated catalyst clearly indicate that the cause of induction period was not due to changes in the dispersion of the supported Pd during the induction period, since H_2 treatment would not cause a redispersion of the Pd.

Because of the nature of the catalyst precursor ($PdCl_2$) used to prepare the Pd/SiO_2 catalyst under investigation, the induction might be thought to occur as a result of the removal of residual Cl^- from the catalyst surface. Iyagaba *et al.* (22) found this to be the case for Ru/SiO_2 during CO hydrogenation, probably as a result of the formation of H_2O. The results shown in Fig. 12 clearly discount this possibility since both the fresh and the used (regenerated) catalysts gave the same time-on-stream results for MeOH synthesis reaction. Miura *et al.* (23), in fact, have shown that treating Pd/Al_2O_3 with H_2 at 230°C before reaction removes all Cl^- from the catalyst. This does not mean that using a Pd precursor containing Cl^- ions would not have any impact on the activity of these catalysts for MeOH synthesis. On the contrary, it has been shown (12, 24, 25) that catalysts prepared using $PdCl_2$ have more activity than ones prepared from $Pd(NO_3)_2$. However, it can be concluded that removal of Cl^- is not the cause of the induction period.

The conversion of CO dissociation sites into sites which stabilize CO in a molecular form and permit it to react with hydrogen to produce MeOH (13) could be another possible reason behind the induction phenomenon. However, in this case, for Pd/SiO_2, the increase in MeOH synthesis rate cannot be explained by a conversion of CH_4 synthesis sites to MeOH synthesis ones since little CH_4 was formed, even initially.

Obviously, Pd can store a significant amount of hydrogen interstitially. Thus, it might be hypothesized that the induction effect is due to excess hydrogen being present on/in the Pd particles after reduction and at the start of reaction. This, however, does not seem to be the case. An induction period was detected even after heating the catalyst for 2 h

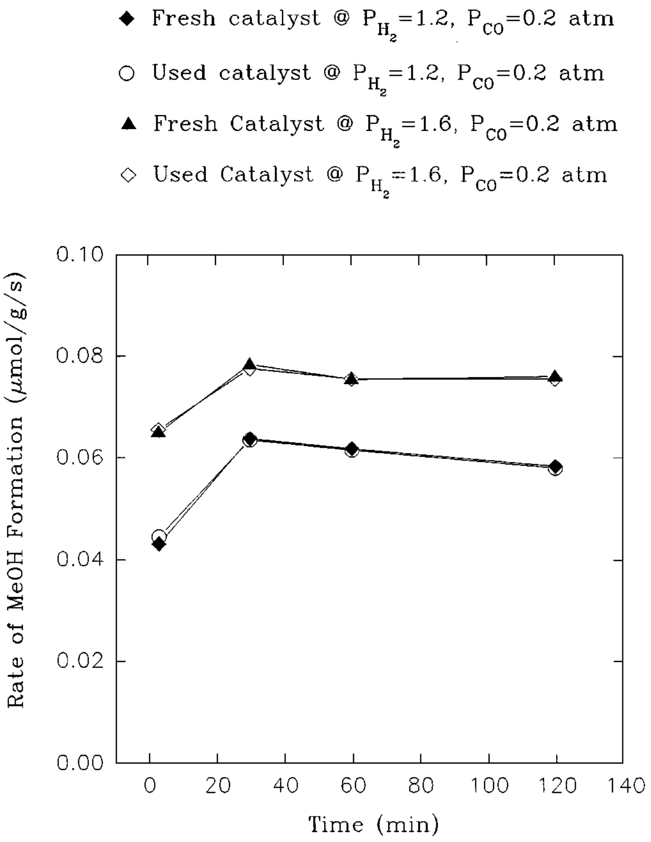

FIG. 12. Rate of formation of MeOH vs time-on-stream for fresh and used (regenerated) catalysts at two different partial pressures of H_2 (at 220°C).

at 450°C in flowing He after reduction and prior to reaction (28).

Another possible cause of the induction phenomenon could be the modification of the Pd particles by H_2O or CO molecules forming Pd–O species that would enhance the capability of Pd for the formation of MeOH. However, it is unlikely that such Pd–O species would be stable enough during the reaction, given the high relative partial pressures of H_2 used.

Driessen *et al.* (15) have argued that the modification of the active sites for the formation of MeOH is not caused by carbon deposition on the active catalyst surface. They have suggested that the stabilization of $Pd^{\delta+}$ species in the vicinity of Pd^0 species is likely the reason behind the induction phenomenon. This latter argument cannot be completely ruled out based on the data presented here, although an increase in the amount of $Pd^{\delta+}$ with increasing P_{H_2} would not seem likely.

Finally, it is possible that the increase in MeOH surface intermediates (and probably in the number of active sites) during the induction period might be related to the formation of Pd carbidic species that take some time to form. This possibility, unfortunately, cannot be examined by XRD because of the small Pd particle size. However, the amount of surface (and perhaps bulk carbon) can be inventoried using stop-flow measurements, where the reaction mixture is replaced at a given time by H_2. Table 4 shows the results for the stop-flow experiments done at two different partial pressures of H_2 (0.8 and 1.6 atm) but the same partial pressure of CO (0.2 atm) and temperature (220°C) for 3, 30, and 120 min reaction. No additional carbon was able to be removed after performing the stop flow experiments at 220°C on heating up to 400°C in H_2. At the lower partial pressure of H_2 (0.8 atm) the amount of carbon deposited, as determined by the stop-flow measurement, increased during the induction period and then leveled off (within experimental error). Obviously, much of the intermediates and adsorbed MeOH desorbed during the 5 min He flush before H_2 flow was resumed. In addition, some of the carbon coming off during stop-flow may have been potential MeOH intermediates stopped in the early stages of formation. However, there is not a direct correlation between the amount of carbon removed during the stop-flow experiments and the amount of MeOH intermediates (N_{MeOH}). Less carbon was apparently deposited at the higher H_2 partial pressure while under these conditions N_{MeOH} was much larger. It is suggested that the difference in the amount of carbon at the different partial pressures of H_2 is probably due to a more effective hydrogenation of the surface carbon-containing species at the higher partial pressures of H_2.

Ziemecki and Jones (26) have found that, by exposing Pd black to ethylene at 200°C, a Pd–C phase is formed which they suggested to be an interstitial solution of C in Pd. However, Ziemecki *et al.* (27) have found that such a Pd–C phase is not stable at operating temperatures of 150°C in the presence of H_2. Although this last finding does not perhaps exclude the possibility of a surface Pd–C species, preliminary experiments have shown that depositing carbon on the surface of Pd/SiO_2 prior to reaction (from either ethane or CO) did not alter the existence of an induction period observed for MeOH synthesis. Thus, even though this induction phenomenon is not simply related to surface carbon, it is possible that some sort of Pd–C interaction may act to form/stabilize additional active reaction sites for MeOH synthesis during the induction period as evidenced by the increase in the concentration of active surface intermediates, N_{MeOH}.

TABLE 4

Stop-Flow Results at 220°C for Pd/SiO_2

Reaction conditions before stop-flow		Amount of surface carbon removed (μmol/g)[a]		
P_{H_2} (atm)	P_{CO} (atm)	After 3 min reaction	After 30 min reaction	After 120 min reaction
0.8	0.2	0.3	1.0	0.8
1.6	0.2	0.1	0.3	0.2

[a] Maximum error ±10%.

CONCLUSIONS

Induction occurred in the rate of MeOH synthesis over a Pd/SiO_2 catalyst for all operating conditions investigated. The induction period was in all cases within 30 min of the start of reaction and seemed to be unaffected by the reaction conditions (H_2/CO ratio) except in magnitude of effect. However, the induction phenomenon was more significant for the catalyst under conditions giving low initial activities for MeOH synthesis.

During the induction period, a significant increase in the number of surface intermediates leading to MeOH was found to be the cause for the increase in the MeOH synthesis rate. On the other hand, the pseudo-first-order intrinsic activity of the sites leading to MeOH ($k^0 = 1/\tau^0_{MeOH}$) was found to be constant, within experimental error, during the induction period. The SSITKA parameters (N_{MeOH} and τ_{MeOH}) were able to be corrected for readsorption of MeOH by extrapolation to space time = 0, equivalent to an infinite flow rate through the catalyst bed.

The observed induction phenomenon in MeOH synthesis rate is concluded to not be caused by changes in the dispersion of the SiO_2-supported Pd particles, by the removal of residual Cl^- ions, by the presence of initial surface or bulk hydrogen, or by the transformation of CH_4 synthesis sites into MeOH synthesis ones. In addition, the stabilization of $Pd^{\delta+}$ in the vicinity of Pd^0 would also not seem likely to be the cause. Some involvement of carbon deposition may be postulated as a cause; however, if this is the case, it is not simply the deposition of carbon.

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