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Complete methane oxidation over Pd catalyst supported on α-alumina. Influence of temperature and oxygen pressure on the catalyst activity

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Abstract

The influence of the reaction parameters including temperature, oxygen concentration, and of in situ hydrogen reduction on the Pd catalyst activity towards complete methane oxidation is studied experimentally.

Zero porosity α-alumina plates are used as a support for Pd catalyst. This lowers the influence of metal–support interaction on the catalyst state as confirmed by UV–visible spectroscopy. A plug flow reactor with a high linear gas velocity is used to measure the reaction rate. Overall conversion is kept low for most of the experiments so that the reaction is in the kinetically limited regime. The oxidation state of the catalyst before and after the reaction is determined using UV–visible reflectance spectroscopy of the plate surface. Changes in the catalyst activity with time are monitored after stepwise changes in the reaction parameters.

Activity was found to decrease with time at low temperatures and high oxygen concentrations (condition when PdO phase is stable) and to increase with time at high temperatures and low oxygen concentrations (conditions when Pd is stable). A sharp increase in conversion was observed after the in situ hydrogen reduction of the sample.

The experimental data is consistent with the reduced Pd form of the catalyst being more active towards methane oxidation than the oxidized PdO form at high temperatures. Possible particle size and morphology effects are discussed. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Palladium supported on aluminas has been found to be the most promising catalytic system for the complete oxidation of methane [1]. Numerous studies of this catalytic reaction have been carried out in recent years [2–19]. A summary of selected data from the literature on complete methane oxidation over alumina-supported Pd catalyst is provided in Table 1. In spite of the intensive research of the system, there is still a lack of agreement on many questions concerning the catalyst behavior during the reaction. The activation energy for the reaction reported in different works varies by a factor of 3 and the pre-exponential coefficient varies by orders of magnitude. There is also no consensus on the mechanism of the catalytic process. Many groups [2–15] conclude that the reaction is structure-sensitive, but others [16,17] argue that at high coverage, when a particulate phase of the catalyst is formed, the reaction ceases to be structure-sensitive. There is also no agreement on which state of the catalyst is more active for methane oxidation at high temperature conditions. Oh et al. [9,10],

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Table 1

Reference	Catalyst composition	Reactant mixture	Particle size (nm)	Temperature range (C)	Turnover frequency (s^{-1})		Activation energy (kcal/mol)	
					Low	High	Low	High
Baldwin and Burch [4]	5 wt% Pd/	CH_4:O_2=1:20		270–470				
	γ-Al_2O_3		2–70		0.428	3.4	19.1	37.0
	δ-Al_2O_3	1% CH_4/air	5–75		7.02	67.7	16.7	23.9
	γ-Al_2O_3		5.4		17.5	5.4	19.3	
	γ-Al_2O_3		8.8		41.3		19.2	
	γ-Al_2O_3		2.1		0.466		28.8	
Baldwin and Burch [3]	0.88–3.19 wt% Pd	CH_4:O_2=1:20		275–450				
	γ-Al_2O_3 (Cl)		1.6–4.1		1.19	4.54	19.2	25.7
	γ-Al_2O_3 (N)	1% CH_4/air					17.0	19.2
	SiO_2 (N)		9.4–18.5		2.37	19.7	24.1	31.5
Cullis and Willat [17]	2.7 wt% Pd/Al_2O_3	CH_4:O_2 from 1:10 to 10:1	14–80	230–530			8.4	19.8
	Pd/Al_2O_3						5.5	20.1
	Pd/TiO_2	1% CH_4/air					10.8	21.2
	Pd/TiO_2						8.1	20.3
Drozdov et al. [18]	Pd/Al_2O_3		<5	400–500			22.9	
	Pd black						14.3	
Anderson et al. [1]	0.5 wt% Pd/Al_2O_3	CH_4:O_2=0.66:40 not diluted		300–450			21.8	
Hicks et al. [14,15]	0.2–0.5 wt% Pd/Al_2O_3	CH_4:O_2:He=1:2.2:18		260–370				
	Dispersed particulate	P_t=1060 Torr	1–17		0.02	0.06	27.0	
			1–3.3		1.2	5.6		29.0
Yao [19]	0.038 wt% Pd/Al_2O_3	CH_4:O_2:He=1:0.1:98.9	1.6–6.4	250–500	0.012	0.31	17	20
	Pd wire	1:4		350–500	5.4		17	
Ribeiro et al. [16]	1–10 wt% Pd/Al_2O_3	2% CH_4/air	2–110	240–400			18	22
	Pd/ZrO_2				0.02	0.08		
	Pd/Si-Al_2O_3							
Farrauto et al. [7,8]	4 wt% Pd/γ-Al_2O_3	1% CH_4/air		300–800				
Primet and Briot [5]	1.95 wt% Pd/γ,δ-alum	CH_4:O_2:N_2:=1:4:95	5-fresh 16–20	200–500	Increase 20 times in r×n		18	24

Hicks et al. [14,15] argue that the reduced Pd form is more active, while Burch et al. [2–4], Farrauto et al. [7,8], Primet et al. [5,11,12] and McCarty [13] consider the metal phase to be less active or completely inactive.

These many differences in conclusions by different investigators suggest that the Pd/alumina system has a complex behaviour. We can assume that the catalyst activity depends not only on the preparation method but also on the reaction conditions. From the data reported in literature and from our experience with the catalyst the following problems which complicate the analysis of the system are observed.

- Rapid Pd↔PdO transformation: Pd catalyst supported on alumina can easily undergo a phase transformation between the metallic Pd and the oxidized PdO state during the reaction. The oxidized form of the catalyst is stable at low temperatures and the reduced form is stable when the temperature is increased. The change in the oxidation state leads to a change in both the crystal structure and the electronic properties of the catalytic surface. Therefore, it can lead to the change in the catalyst activity. Another ambiguity comes from the fact that the phase transformation of the palladium catalyst, especially surface oxidation, can occur very rapidly. The catalyst can change its state under the reaction conditions as well as during the preheating stage of the experiment or during cooling down after the process. Precautions should be taken to ensure that the state of the catalyst, determined by various methods before or after the reaction run, is the same as it was under the reaction conditions when the activity measurements were performed.
- Influence of the reaction conditions on the catalyst state: many reaction parameters, such as gas phase composition and pressure, type of support, additives and contaminants, pretreatment history, can influence Pd↔PdO transformation. This makes it necessary to provide control over all of these parameters during the reaction and to run the reaction under conditions were only one parameter is changing with time.
- Pd/support interaction and possible Pd aluminate formation: interaction between the catalyst particles and the support can become another factor influencing the behavior of the catalyst. For Pd supported on high surface area (HSA) γ-alumina this interaction can become a strong factor influencing the catalyst behavior and can also vary during the process as the alumina transforms at high temperature reaction conditions. Formation of Pd aluminate in such a system was reported in work by Otto et al. [20] and was noted in our work by appearance of high absorption in UV–visible spectra at the wavelength around 250 nm.
- Hydrogen penetration into the bulk of Pd crystallites: hydrogen is easily dissolved into the bulk of solid palladium. Therefore, hydrogen adsorption used for the experimental measurement of the number of "active sites" on the catalyst surface will not necessarily yield an accurate representation of the surface.
- Particle size and number of active sites change in the reaction: the works of Ruckenstein and Chen [21,22] suggest that the particle size can change during the reaction. Furthermore, it can not only increase due to particle sintering but also decrease in some conditions due to break up of the particles. This means that the effective Pd surface area and the number of active sites are varying during the reaction at different reaction conditions.
- Reconstruction of γ-alumina support at high temperature can block most of the catalyst inside the pores. This can significantly decrease the catalyst surface available for the reaction gas mixture and, therefore, drastically decrease the apparent activity of the catalyst at high temperature reaction conditions.
- Gas diffusion in the pores can limit the reaction. Hot spots can form in the packed bed reactor.
- Oscillations in the catalyst activity noted in large scale prototype test even when all reaction parameters were kept constant. This suggests the existence of some positive feedback in the system.

In the majority of studies reported in the literature the catalyst activity was measured with the reactor temperature varied through the wide intervals in a short time. But the process of the catalyst oxidation/reduction is itself a complex chemical solid state reaction, which includes formation/decomposition of PdO, oxygen adsorption–desorption on the surface and oxygen diffusion through the solid phase. The rate of the catalyst transformation should also strongly depend on temperature [23]. The change in the catalyst oxidation state of the bulk of the crystallites can progress slowly at low temperatures, while it will be almost immediately at high temperature. Therefore, the rate of the temperature ramp itself can cause a difference in the reaction behavior observed in such an experiment.

The goal of this work was to determine which state of the palladium catalyst: the oxidized PdO or the metallic Pd is more active towards complete methane oxidation and how this depends on the reaction parameters. If not only catalyst preparation, type of support and precursor, but also the reaction condition affect the catalyst activity, then this knowledge will allow to predict the most favorable conditions in which the catalyst should operate in different technological devices. Three different experimental procedures were employed to address the problem. Catalyst activity change was studied as a response to the (1) change in the process temperature; (2) variation in oxygen concentration in the gas mixture; (3) in situ hydrogen reduction of the sample. When the parameters of the reaction system, such as the temperature or the gas composition, are changed, two parallel effects can be observed. Firstly, the conversion will change due to the nature of the chemical reaction (exponential dependence on temperature and power dependence on reagents concentration). Secondly, the catalyst structure can change leading to a change in the specific catalyst activity and, hence, to the observed methane conversion. To distinguish between these two effects in this study the reaction parameters were varied stepwise and the subsequent change of the reaction rate with time was monitored as a response to the change in the reaction conditions. The change in methane conversion caused by the first factor (change in the reaction rate assuming that catalyst is not modified) should appear almost immediately after the parameters were changed. A slow shift in conversion with time when all reaction parameters are kept constant after stepwise change of one of them can, therefore, be attributed to the slow modification of the state of the catalyst (bulk oxidation–reduction, particle size, morphology) under new conditions.

To minimize the influence of metal–support interaction on the experimental results low-surface-area (LSA) α-alumina support is used in this work.

2. Experimental

2.1. Sample preparation

Pure α-alumina plates with zero porosity were used as a support for the catalyst in all experiments described in this work. The plate surface was covered with Pd using aqueous $Pd(NO_3)_2$ solution as a precursor. The salt was dissolved in water and ammonia was added to prevent coalescence. The stock solution had concentration of the order of 0.4 mg Pd/ml. Before deposition this solution was further diluted with butanol, to decrease its surface tension and achieve better wetting of the alumina surface. The following procedure was used to cover the plate. A thin layer of the final solution was placed on the hot surface of the plate. It dried instantly and then the salt was decomposed in the furnace air at 550°C giving a very low PdO coverage of the surface. This procedure was repeated many times to obtain the desired amount of Pd on the plate. Finally, the plate was calcined at 550°C in the furnace air overnight. This procedure allows to have a uniform coverage of the plate where all the metal particles stay on the top surface of the plate and are easily available for the reaction gases.

2.2. X-ray microprobe technique for measurement of surface coverage

X-ray microprobe technique was employed to measure the Pd surface coverage of the sample. The intensity of the characteristic X-ray signal from the tested surface was compared with that from a standard reference prepared by vacuum deposition of a 100 Å Pd layer on a clean alumina plate. The ratio between these signals equals to the ratio of Pd layer thickness between the sample and the standard and the surface coverage the sample could be determined by these measurements. The average Pd layer on the sample plate was found to be 30–50 Å, which corresponded to the metal coverage of $\sim 5\times 10^{-6}$ g Pd/cm^2. Knowing the surface area of the plate, which was exposed to the reaction mixture (5 cm^2), the total amount of Pd in the reaction could be calculated, which was on the order of 10^{-4} g.

2.3. *UV–visible reflectance spectroscopy*

The UV–visible reflectance spectroscopy was used to distinguish between the oxidized and the reduced states of the catalyst. The adsorption edge appears in reflectance spectrum of PdO in the visible part of the diffuse between 500 and 600 nm due to the semiconductive electronic structure of crystalline PdO, which disappears when the catalyst reduces to the metallic Pd state [24]. This allows to distinguish between the two oxidation states of the catalyst. As the wavelength of the light used for spectroscopy (200–800 nm) is much longer than the catalyst particle size (less than 100 nm), the crystal state averaged over the whole volume of the particles is measured by the method. We should note here that in spite of this technique been not surface sensitive in general, for small catalyst particles of the order of 10 nm, which is a usual size with supported catalysts, even 2–3 layers of crystalline PdO on the surface of the particle will involve ca. 30% of the whole volume and should provide an edge distinguishable in the absorption spectrum.

In Fig. 1 the UV–visible spectra of samples after a standard pretreatment are shown. Curve 1 shows the spectrum of the plate sample calcined in air at 550°C overnight. The absorption edge between 500 and 600 nm demonstrates that the catalyst is in the PdO state. Curve 2 shows the spectrum of the sample reduced in hydrogen at 500°C for 1 h. The edge disappeared which indicates reaction to the metallic Pd state of the catalyst. The Curves 3 and 4 demonstrate the spectra from two parts of the same sample, which was heated to 900°C in the furnace air for approximately 1 h (PdO thermally decomposes at this temperature in air). Curve 3 shows the spectrum from the part which was quenched and demonstrates that the catalyst was reduced to metallic palladium during the procedure. Curve 4 shows the spectrum of the part which was cooled slowly in the furnace (for approximately 2 h). Reappearance of the absorption edge on this spectrum shows that reoxidation of palladium, though not complete, started during the cooling of the sample. We can conclude that the timescale of the bulk Pd→PdO transition is of the order of 30 min at temperature near 700°C.

The timescale of the opposite process of the PdO thermal decomposition is demonstrated in Fig. 2. The plate sample in the initial PdO state was repeatedly placed into the furnace preheated to 900°C, kept there for short periods of time, which are indicated in the figure, and then quenched to room temperature. The UV–vis spectra from the sample after each treatment are shown in the figure. We see that after each treatment more of the sample is reduced to the metallic Pd state. After a total period of time of 10 min in the furnace the spectrum demonstrates almost complete reduction of the sample. The PdO decomposition at high temperature occurs on the timescale of minutes.

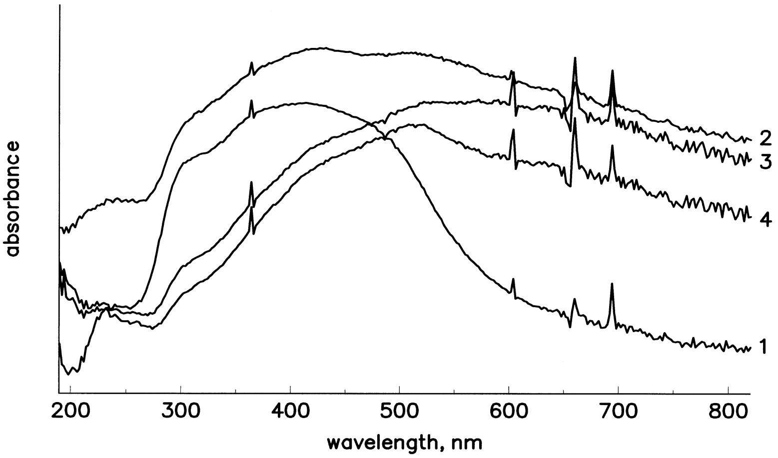

Fig. 1. UV–visible spectra from samples after standard preparation and procedures. (1) PdO state, sample calcined in air at 550°C overnight; (2) Pd state; sample reduced by hydrogen at 500°C for 1 h; (3) Pd state; sample calcined at 900°C in air for 1 h and quenched; (4) Pd reoxidation; sample no. 3 cooled slowly in the furnace for 2 h.

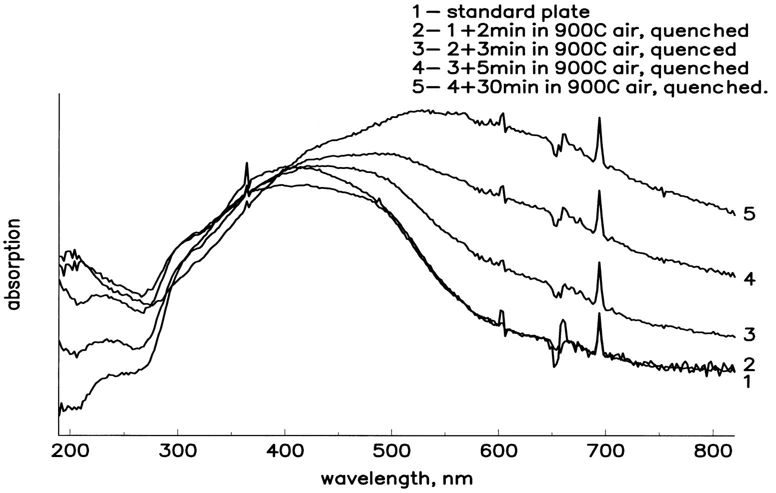

Fig. 2. PdO reduction timescale. 900°C in furnace air. Sample is repeatedly introduced into the furnace for short intervals of time and quenched.

This illustrates that the catalyst can change its phase before or after the reaction rate measurements are performed. Therefore, precautions should be taken during preheating of the sample to the reaction conditions and during subsequent cooling down in order to avoid artifacts due to change in the catalyst state.

Reflectance UV–visible spectroscopy of the catalyst surface can also provide information on the particle size change during the reaction. For the PdO particles of the order of nanometers the light absorbance depends on the particle size, so that the shift in the position of the absorption edge will show how the particle size changes during the process.

2.4. *TEM study of the model sample*

A thin layer of γ-alumina is supported on the gold TEM grid and Pd is deposited on this surface from the same solution as for the standard plate samples. The grids are treated under different conditions similar to that used for the reaction of the plate sample. TEM observations of the catalyst particles after different treatments showed that the particle size after the preparation and calcination in furnace air at 550°C overnight was of the order of 3–5 nm. After hydrogen reduction at 500°C for 1 h it was again found to be 3–5 nm. So, at least for small PdO particles and moderate temperatures we did not observe any change either in particle size or morphology after hydrogen reduction. After treatment in the reaction with 1% methane/4% oxygen/nitrogen at 600°C the particle size was found to increase to 30–50 nm in the time interval of 15 h.

2.5. *Measurement of the catalyst activity*

A schematic drawing of the reactor is shown in Fig. 3. The gas mixture composed by gas flow controllers is passed through a narrow gap (0.1–1 mm thick) over the catalyst surface (15 mm wide, 40 mm long). This provides high linear velocity of the gas flow and ensures the kinetically limited regime of the reaction. The composition of the gas mixture after the reactor is measured by the GC with FID and methanizer, so that concentration of CH_4, CO, CO_2 can be detected. Total conversion is kept low (below 10% in most experiments) so that the change in the gas mixture composition along the reactor is negligible. The ratio of CO_2 formed in the reactor to the initial methane concentration in the mixture is proportional to the reaction rate and, hence, to the catalyst activity. At the reaction conditions with lean gas mixtures CO production was not observed at any stage of the experiment.

As it was discussed above many parameters of the reactor system can affect the catalyst state and activity. Therefore, our experiments were designed in such a way that all parameters of the system were kept constant and the change in the catalyst activity with

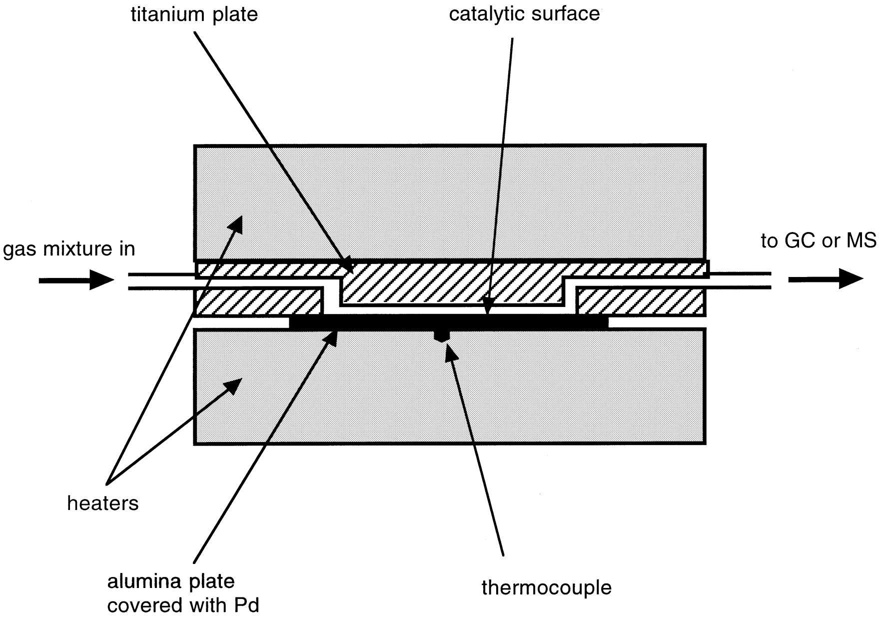

Fig. 3. Schematic diagram of the experimental reactor cell.

time was monitored as a result of change in one of the parameters.

3. Results and discussion

3.1. Temperature dependence of the catalyst activity

In the first set of experiments the effect of temperature on the catalyst activity was studied. In the experimental run shown in Fig. 4 the catalyst plate in the PdO initial state (calcined at 550°C overnight) was preheated to the initial reaction temperature with air flowing through the reactor. This pretreatment ensures the PdO state of the catalyst before the reaction measurements were started. The composition of the gas mixture during this run was: 1% methane/4% oxygen/95% nitrogen. The experimental points in the graph show the methane conversion to CO_2 and the line shows the reactor temperature profile. The temperature of the reactor was initially set to 500°C and kept constant during first 20 h. At this time a decrease in the catalyst activity was observed, which we attribute to the sintering of the PdO particles. On the second step the temperature was increased to 800°C. An initial increase in the methane conversion was observed with increasing temperature. After the temperature was stabilized at the new level the conversion continued to increase and rose from 50% to more than 80% in approximately 10 h. Because all the experimental parameters were kept constant at this time this rise in the conversion can be attributed to the increase in the catalyst activity with time. On the final step the reactor temperature was rapidly returned to 500°C. The conversion decreased instantly, though, to a higher level than at the same conditions in the beginning of the run. Then it continued to decrease slowly with time and in approximately 20 h reached the same low level ($\sim$1%) as at the end of the first step, before the temperature rise.

UV–visible spectra of the sample at different stages of the experiment, shown in Fig. 5, demonstrate that the catalyst was in the oxidized PdO state after the first and the last steps of the reaction, while it was in the reduced Pd state after the second step at a high temperature. This experiment demonstrates that at high temperature the catalyst activity increases with time as the PdO decomposes to the metallic Pd and at the lower temperatures (500°C), where the PdO state

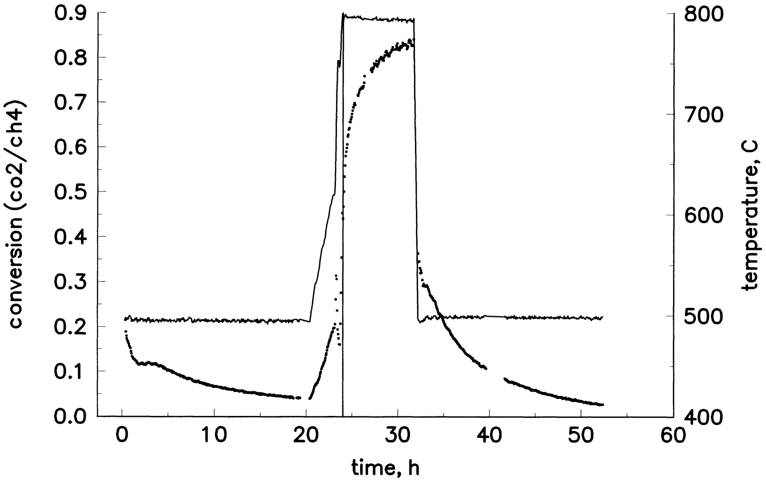

Fig. 4. Variation of the catalyst activity at different temperatures. 1% CH_4/4% O_2/nitrogen; contact time τ=2.5 s. Experimental points show the methane conversion to CO_2, line shows corresponding temperature profile. Catalyst oxidation state is PdO in the beginning and at the end of both steps at T=500°C, Pd at the end of the step at T=800°C.

of the catalyst is stable, the activity decreases with time as the Pd reoxidizes to the PdO and the PdO sinters into larger crystallites.

In our experiments it was found that under the experimental conditions. i.e. 2–3% methane in air, the threshold temperature is approximately 760°C. Above this temperature the catalyst activity is increasing with time and below this temperature it is decreasing with time. The experimental run in Fig. 6 demonstrates that when the catalyst in the PdO state was set into reactor at a temperature higher than 760°C, the methane conversion was increasing with time from the beginning of the experiment. The rate of activity increase became higher as the temperature was increased on the second step shifting the system further from equilibrium. Finally the activity reached a stable plateau, when the PdO phase completely decomposed into the metallic Pd form.

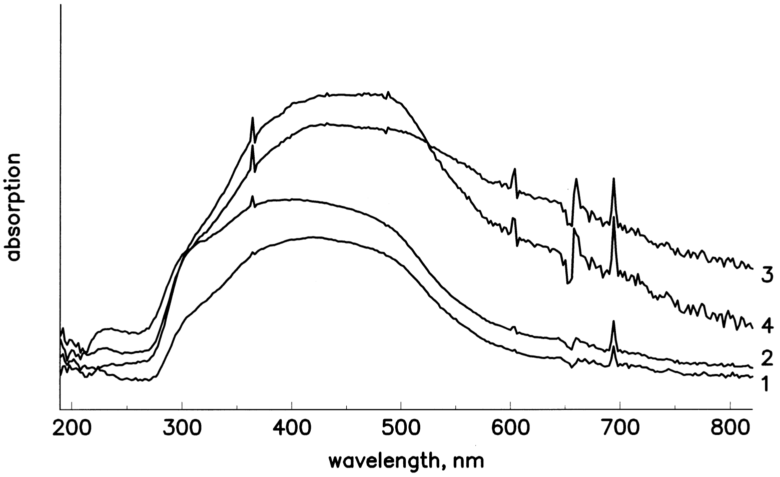

Fig. 5. UV–visible spectra from the sample in Fig. 4 at different stages of the reaction. (1) Fresh sample; (2) after the first stage (500°C); (3) after stage at 800°C; (4) final state (500°C).

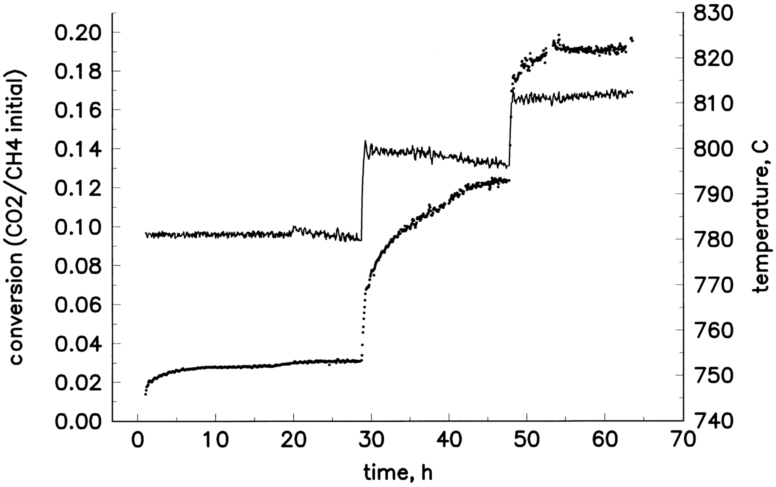

Fig. 6. Variation of the catalyst activity at different temperatures. 2% methane/air; contact time τ=0.1 s. Catalyst oxidation state is PdO in the beginning and Pd at the end of the run.

This suggests that the equilibrium between the reduced and the oxidized forms of the Pd catalyst exists under the described reaction conditions at the temperature 760°C. Below this temperature the PdO form is thermodynamically stable and the apparent catalyst activity is decreasing with time due to oxidation and sintering. Above this temperature the Pd form is more stable and the catalyst activity increases with the reduction of the PdO crystallites.

3.2. *Activity dependence on oxygen pressure*

In the following experiments the dependence of the catalyst activity on the oxygen pressure in the gas mixture was studied. The Pd⇔PdO equilibrium at the reaction conditions should depend both on temperature and on the oxygen partial pressure in the gas phase over the surface. At constant temperature near the threshold at 760°C decreasing the oxygen pressure over the surface would shift the equilibrium towards the metallic Pd phase and increasing the oxygen pressure would shift the equilibrium towards the oxidized PdO phase. In the next run shown in Fig. 7 the oxygen concentration in the gas mixture was decreased step by step from air down to 4%, while the surface temperature and all other reaction parameters were kept constant. We should note here that all literature data indicate the complete methane oxidation reaction in the presence of excess oxygen to have zero order with respect to oxygen. This means that the reaction rate and, hence, the observed methane conversion should not change when the oxygen concentration in the mixture is changed. This was confirmed in these experiments as with each step of oxygen concentration decrease no immediate change in methane conversion was observed. Therefore, the slow change in conversion observed on each step of the experiment can be attributed to the change in the catalyst activity which is caused by the decrease of oxygen pressure in the gas phase over the catalyst surface.

In the beginning of the run the PdO form of the catalyst is stable and the decrease of activity with time is observed. The decay continues, though at a lower rate, before the oxgyen concentration in the mixture was decreased to 12%. After that a gradual increase in conversion begins. With further lowering of the oxygen concentration to 8% and 6% (stoichiometric composition) this increase becomes faster as the Pd⇔PdO equilibrium is shifted more and more towards the metallic state. When the oxygen concentration in the mixture is lowered to 4% (below the stoichiometric), a sharp increase in conversion is observed (high level of CO production is also observed in this step). In the next step the oxygen concentration is returned to 6%. The conversion

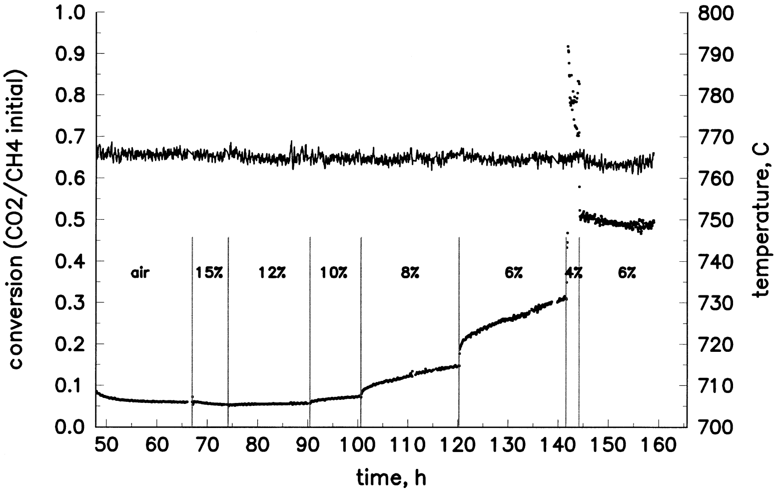

Fig. 7. Oxygen pressure variation. 3% CH_4; contact time τ=0.9 s; T=760°C. Numbers show the percent of oxygen in the gas mixture. Initial state of the catalyst – PdO, final state – Pd [27].

dropped instantly, but to a new level which was higher than that on the previous step with 6% oxygen. Conversion also remained almost constant with time which is consistent with the previous observations that metallic Pd is significantly more resistant to sintering than the PdO. UV–visible spectroscopy shows that the catalyst was in the reduced state at the end of the run.

The results of the same procedure carried out at a temperature T=710°C are shown in Fig. 8. At this lower temperature the PdO state of the catalyst is stable at considerably lower oxygen pressures. The increase in the catalyst activity started only when the oxygen concentration in the mixture was lowered to 2% (half of stoichiometric). On the steps with 1.5% oxygen in the mixture the sharp increase in the conversion and CO production were observed again (similar to the behavior at 4% oxygen at 760°C). When the oxygen concentration was returned to the stoichiometric 4%, the catalyst activity was high (much higher than that for the step with 4% oxygen before reduction) and stable. But as the oxygen concentration was set at 16% at the end of the run, a decrease in the catalyst activity with time was observed during last 20 h of the reaction run. The formation of the PdO absorption edge was observed in the UV–visible spectrum of the sample after the end of the experiment which indicated that the reoxidation process was going in the last step.

The results of these two experiments with decreasing oxygen partial pressure show again that as the reaction conditions are modified in such a way that the Pd state of the catalyst becomes more stable (high temperature, low oxygen concentration), the increase in the catalyst activity with time corresponding to the PdO→Pd transformation occurs. When the conditions are modified in such a way that the PdO form of the catalyst is more stable (lower temperature, high oxygen pressure), the decrease in the catalyst activity with time corresponding to Pd→PdO transformation and particle sintering is observed.

It was found that the initial decay in the activity when the PdO state of the catalyst was stable has a negative first order with respect to time. We attribute this decay, which was observed with both types of experimental procedures, to sintering due to PdO particle migration over the α-alumina surface. We should note that in the reaction conditions where the Pd state of the catalyst was stable, i.e. at the high-temperature region in the first set of experiments (800°C in Fig. 4 810°C in Fig. 6) and on the low-oxgyen concentration steps after catalyst reduction in the second set of experiments (final 6% O_2 in Fig. 7 and second 4% O_2 in Fig. 8), the catalyst activity remained almost constant with time, demonstrating very small sintering of the catalyst in the metallic Pd state. This observation suggests that the metallic Pd state of the catalyst is much more stable against

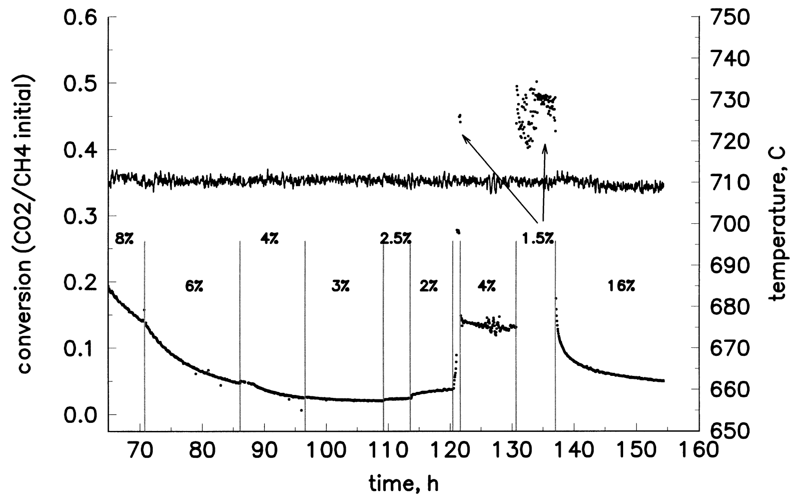

Fig. 8. Oxygen pressure variation. 2% CH_4; contact time τ=0.3 s; *T*=710°C. PdO initial state, Pd/PdO final state [27].

deactivation, which can be explained by formation of large Pd crystallites with active low-index surfaces [25]. This change in morphology can be one of the reasons for the apparent catalyst activity increase during the reduction process.

3.3. In situ hydrogen reduction

In the next experiment, shown in Fig. 9, transformation in the catalyst state was achieved by in situ hydrogen reduction of the sample under conditions where otherwise the PdO form of the catalyst was stable. The reactor was preheated to 600°C while the mixture of 10% hydrogen in nitrogen was flowed over the sample, so that the catalyst was in the reduced Pd state before the reaction. The gas mixture of 2.5% methane in air was used on all stages of the run. Similar to the results observed in the previous experiments, the methane conversion decreased gradually as the reaction parameters were kept constant, which again suggests a decrease of the catalyst activity as the Pd oxidizes to PdO. After the initial decay of the catalyst activity during ~10 h on stream, the reaction gas mixture was cut off from the reactor and the mixture of 10% H_2 in nitrogen was flowed over the sample for 15 min after which time the reaction was resumed. A sharp near ten-fold increase in the catalyst activity was observed as the same gas mixture was reintroduced into the reactor and all other parameters were the same as before the hydrogen reduction. This can be attributed to an increase in catalyst apparent activity caused by the reduction, which might include particle size and morphology changes. During the following time interval (~10 h) at *T*=600°C the catalyst was reoxidizing to the PdO state, causing the methane conversion to decrease again. The temperature was then lowered to 550°C in approximately 30 min while gas mixture was flowed over the catalyst and the methane conversion measurements were taken. The N_2+H_2 mixture was again introduced into the reactor for 15 min after which time the reaction at a constant temperature *T*=550°C was resumed. This process was repeated at 550°C, 500°C, 450°C, 400°C, 350°C and 300°C (the times at which each hydrogen reduction of the sample occurred are shown by the vertical lines in Fig. 9). In each step (except the step at 300°C, where only a small increase in conversion occurred) more than a ten-fold increase in conversion after the reduction was observed, followed by a gradual decrease to a low level in approximately 10 h. As the reaction parameters (reaction mixture composition, reactor temperature, gas flow rate) before and after the reduction on each step were the same, the change in conversion can be attributed to a change in the catalyst activity.

After the last step of the reaction run (*T*=300°C), the temperature of the reactor was gradually increased back to 600°C with the ramp ~1.5°C/min. On the

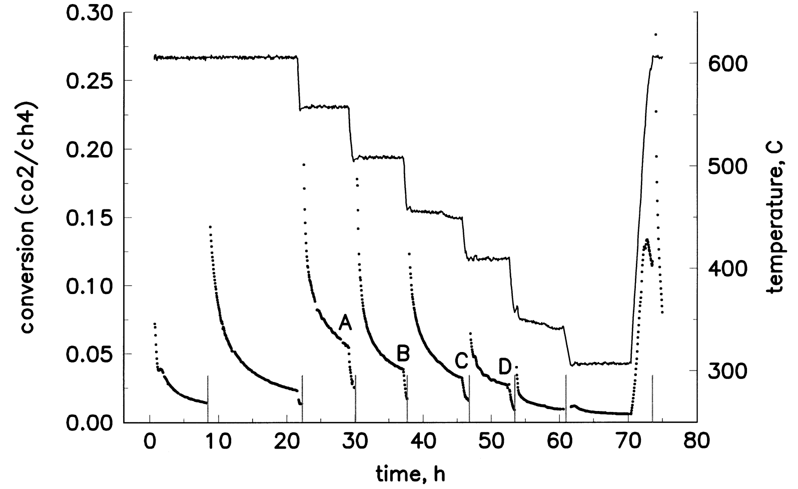

Fig. 9. In situ hydrogen reduction of the catalyst. 2% methane/air; contact time τ=0.3 s. Vertical lines represent times when the catalyst was reduced by H_2+N_2 mixture for 15 min at the given reactor temperature.

temperature interval up to 500°C the conversion was increasing as is normal for an activated reaction, but above this temperature it started to decrease as the temperature was still rising from 500°C to 600°C. Thus, the apparent activation energy was found to change from positive to negative around 500°C. In a separate experiment it was found that oxidation of Pd at 300°C is a slow process so that the catalyst particles may not be fully reoxidized after 10 h under these conditions. When the temperature is increased gradually, reoxidation of Pd and sintering of the resulting PdO clusters occurs with an increasing rate. At 500°C decreases in the rate of methane conversion due to catalyst deactivation overcomes the rate of methane conversion increase due to the temperature rise and the apparent negative activation energy is observed.

After the temperature reached 600°C and was stabilized at this level, the sample was once again reduced by the hydrogen/nitrogen mixture and then the reaction gas mixture was reintroduced. A sharp increase in the catalyst activity was again observed after the reduction, which suggests that the catalyst reoxidized on the previous step during the temperature ramp. The reaction run was continued for 1 h after the reduction after which time the sample was quenched. The UV–vis spectrum of the sample indicates that the catalyst became partially reoxidized. The decrease in the activity, therefore, corresponds to the catalyst transformation from the reduced metallic Pd to the oxidized PdO state.

During each step of the experiment the temperature dependence of the methane conversion was measured, while the reactor temperature was decreased to the next value. The temperature dependence of the catalyst activity measured during the sample cooling on these steps (parts A–D of Fig. 9) is shown in Fig. 10. The apparent activation energy obtained from the slope of each line varies from 16.4 to 19.1 kcal/mol. As the temperature dependence of the conversion was measured before hydrogen reduction on each step, this activation energy corresponds to the PdO state of the catalyst. Because in every case the activity decay was not complete prior to the temperature dependence measurements, the low temperature points in the Arrhenius plot could be shifted down by continuous catalyst activity decay, providing, therefore, values for the activation energy higher than the real ones. This in particular can be the case with step A, where the activity decrease was still rather fast at the time when cooling was started and the observed activation energy was higher than the other values. The average value for the activation energy obtained from the plots, about 17.5 kcal/mol, is consistent with the low range of activation energy data reported in literature (see Table 1).

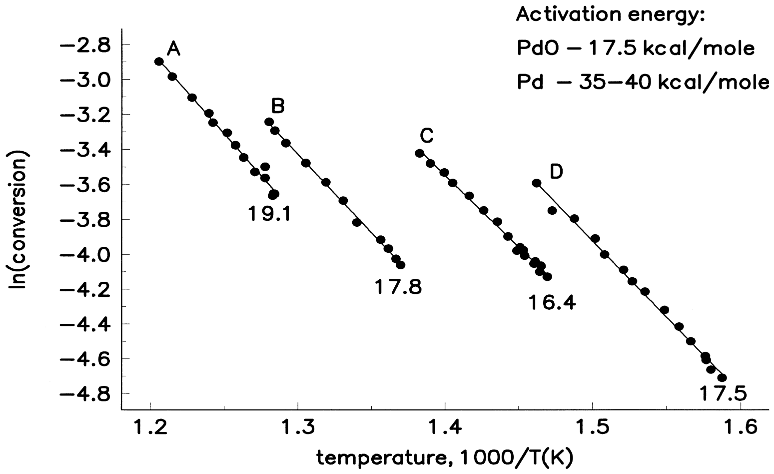

Fig. 10. Temperature dependence of the catalyst activity in the PdO state. Data from the sections of Fig. 9 where reaction temperature was varied, marked as A–D.

In Fig. 11 the temperature dependence of the catalyst activity for the reduced state of the catalysis is shown. The metallic form of palladium is stable at temperatures higher than 700°C, so that the measurements were taken within the high-temperature region. The catalyst was initially reduced in a hydrogen flow at 500°C for 1 h, then preheated to 820°C, and in situ reduced again by passing the N_2+H_2 mixture through the reactor for 10 min. After that the reaction gas mixture flow with 2% methane/8% oxygen/nitrogen was set over the catalyst with the flow rate high enough to yield less than 15% conversion at this high temperature. The temperature of the reactor was decreased slowly from 820°C to 690°C in 3 h time interval, while the methane conversion was measured. At the end of the process the catalyst remained in the metallic Pd state, so that we can assume that Pd was the stable state of the catalyst throughout this experiment. The slope of the line in Arrhenius coordinates gives an activation energy E_a=37.6 kcal/mol, which

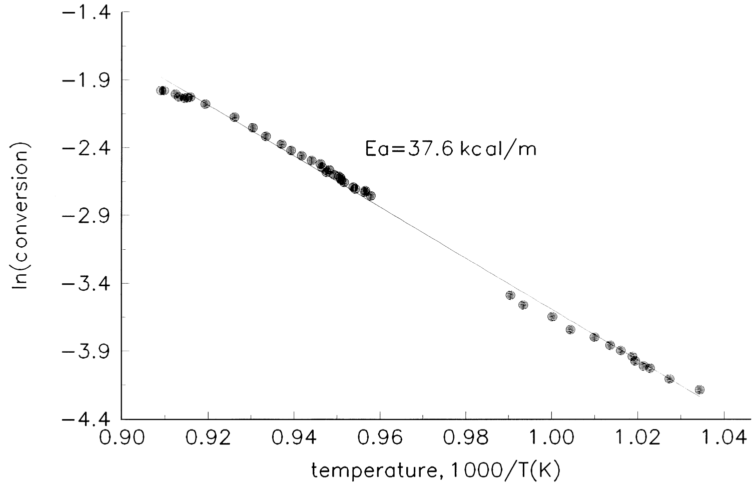

Fig. 11. Temperature dependence of the catalyst activity in the metallic Pd state.

corresponds to the activation energy of complete methane oxidation over the reduced Pd catalysts. This is consistent with the high range of activation energies reported by Baldwin and Burch [3,4] (Table 1).

The activation energy of methane oxidation reaction over the reduced Pd catalyst is found to be approximately two times higher than that for the reaction over the oxidized PdO catalyst. So in our experiments we observed the reaction rate to be higher for the Pd form of the catalyst, in spite of a higher activation energy of the process. This suggests that the pre-exponential coefficient is several orders of magnitude higher for the reaction over the Pd than for that over the PdO state of the catalyst. Comparison of the temperature dependence of methane conversion in low-temperature experiments (when the PdO state is stable) and in high-temperature experiments (when the Pd state is stable and no crystalline PdO can form on the particle surface) corrected with respect to the gas flow rate and the amount of metal yields a ratio of A-factors A_{Pd}/A_{PdO} of the order of 10^5–10^6. Such a large ratio cannot be attributed only to an increase in the particle size during the Pd oxidation process (decrease in surface area is proportional to an increase in the particle size, so that particles should grow five orders of magnitude to account for the change). Differences in the activation energies and the pre-exponential coefficients for methane oxidation over Pd and PdO phases of the catalyst may suggest different mechanisms for the process in each case.

The pre-exponential coefficient depends on many parameters, such as particle size, metal support interaction, poisons, etc., and can change during the course of reaction. For example sintering of the catalyst particles (without change in the oxidation state) would not affect the activation energy, but would decrease the pre-exponential factor, giving an overall decrease in the apparent activity. In the experimental run shown in Fig. 9, where the same samples was sequentially reduced by hydrogen and reoxidized during the catalytic reaction, activation of the catalyst was observed. The methane conversion dependence on the temperature (Fig. 10) gives consistent activation energies on each consecutive cycle, but the lines are shifted to the right (towards lower temperatures) yielding higher pre-exponential coefficients in the Arrhenius expression for the reaction rate. The catalyst, thus, becomes overall more active during this treatment. This increase cannot be explained only by a decrease of the particle size during the process, as this would require the particle size to become more than 100 times smaller after the process. It is possible that morphology can change during the reduction and that dispersed PdO clusters form on the metallic Pd surfaces during reoxidation [26]. This can be one of the mechanisms which account for catalyst activation during the reduction process and higher stability of the Pd phase on the α-alumina support.

All three experimental procedures described in this work demonstrated that reduction of the Pd catalyst supported on LSA α-alumina leads to an increase of its apparent activity. Also, it was found that the activity was either stable or increased when the reaction conditions were favorable for the metallic Pd phase ($T > 760°C$ in 1 atm.air). Overall activation of the catalyst was found in the reduction/reoxidation cycle. All of these phenomena suggest that the particle size and morphology experience a reversible change during reduction/reoxidation, which can at least partially account for the observed change in apparent activity. Further experiments in which careful measurements of the catalyst particle size and morphology by means of SEM, TEM, and electron diffraction on each step of the reduction/reoxidation cycle are planned for better understanding of the system [25,26].

If the methane oxidation over the metallic palladium has higher activation energy and higher A-factor than the reaction over the oxidized form of the catalyst, then at some low temperature the graphs of the temperature dependence of activity in the Arrhenius plot would intersect as sketched in Fig. 12. This means that as the catalyst temperature is decreased, the difference in activity between Pd and PdO states is decreasing and below some threshold temperature (which would depend on the preparation method and pretreatment) the PdO state of the catalyst becomes more active. This can explain the fact that we did not see an increase of the catalyst activity when the sample was reduced at 300°C. Also this can explain the fact that most investigators who used the packed bed reactor system design and carried out the experiments at temperature range of 300–400°C report the oxidized PdO phase of the catalyst to be more active than the reduced Pd form.

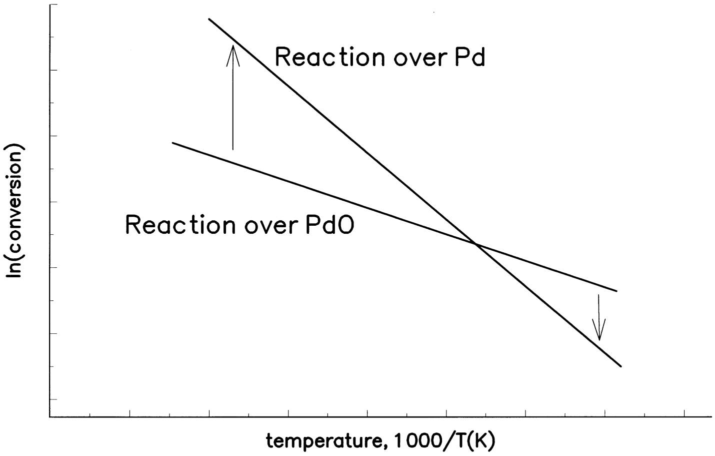

Fig. 12. Comparative activation energies and pre-exponential factors for reaction over the Pd and the PdO catalyst states.

4. Conclusions

Three different experimental procedures have shown that at high-temperature reaction conditions the reduced form of the supported palladium catalyst is more active towards complete methane oxidation than the oxidized form.

The temperature at which the PdO⇔Pd transition occurs depends on the oxygen pressure in the gas phase, the metal–support interaction and other parameters.

The activation energy for complete methane oxidation over the PdO phase of the catalyst can be estimated at 17.5 kcal/mol and over the Pd phase at 35–40 kcal/mol. The pre-exponential factor for the Pd state is 5–6 orders of magnitude higher than that for the PdO state of the catalyst. The pre-exponential factor depends strongly on the process conditions and the history and can change during the reaction.

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