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SSITKA studies of the catalytic flameless combustion of methane

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Abstract

This paper presents results which were obtained for the flameless combustion of methane over the Pd(PdO)/Al_2O_3 catalyst by using the steady state isotopic transient kinetic analysis method. During the reaction switches between $^{16}O_2$/Ar/CH_4/He and $^{18}O_2$/CH_4/He were carried out. The obtained results indicate the presence of large amounts of oxygen as well as of intermediates leading to the formation of carbon dioxide on the surface of the palladium catalyst. Additionally, information was obtained proving that the complete oxidation of methane over Pd/Al_2O_3 catalyst proceeds according to the Mars and van Krevelen redox mechanism. With the increase of the reaction temperature there is an increase in the number of active centres on the Pd(PdO)/Al_2O_3 catalyst surface—a larger amount of oxygen from the lattice of the catalyst is accessible for the reaction of methane oxidation.

Keywords: Oxidation of methane; Flameless combustion; Pd/Al_2O_3 catalyst; SSITKA

1. Introduction

Methane is a major component of the natural gas, which is an important resource utilized all over the world to provide energy. Methane combustion proceeds at high temperatures and leads to the formation of considerable amounts of nitrogen oxides, so that in order to lower their emission many methods preventing their formation or elimination from the exhaust gas are being used. One of the most promising of these methods is the catalytic oxidation of methane [1–4] which permits a significant decrease of the temperature of combustion and, consequently, a reduction of the emission of nitrogen oxides. Additionally, the quantity of carbon oxide is decreased. Moreover, this process can be utilized for the combustion (i.e. removal) of methane from low-concentration mixtures (either for the purpose of obtaining energy or for air purification, e.g. from coal mine post-ventilation air–methane is a greenhouse gas).

For the complete oxidation of methane various kinds of catalysts have been proposed (oxides of transition metals, noble metals, perovskites and hexaaluminates) [1,2,5,6]. The noble metals (palladium, platinum, ruthenium and rhodium), which were placed on the supports with large specific surfaces and good thermo-stability, demonstrated the highest activity [7,8]. On the most active system, the palladium catalyst, the initiation of the reaction occurred at 523 K, while the complete reaction of 2% of methane in a mixture with air could be obtained at 823 K [1]. The palladium catalyst is a very complicated research object, which has been confirmed in many publications [4,9–15]. In spite of intensive studies aiming at finding correlations between the activity of palladium catalysts and their composition and physical–chemical properties, many questions have not yet been answered. During the oxidation of methane over the palladium catalyst, possible transitions Pd ↔ PdO may occur. Both metallic palladium as well as its oxide catalyse methane combustion, although their activities vary. The balance between Pd ↔ PdO under given conditions of the reaction depends on the temperature and the partial pressure of oxygen, while the range of both phases occurring side by side depends on the type of support and the strength of the interaction between the active phase and the support. Most scientists [9,12,16] maintain that metallic palladium undergoes oxidation during methane combustion and that palladium oxide thus produced plays a decisive role in the activity of the Pd(PdO)/Al_2O_2 catalyst. The literature [17] does not provide an unambiguous proposal of the catalytic methane oxidation

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mechanism on the palladium catalyst. In numerous publications there are arguments for both the Eley–Rideal mechanism [18] and the Langumir–Hinshelwood mechanism [19,20], or the Mars and van Krevelen redox mechanism [21,22].

This paper presents investigations proving that this process proceeds according to the Mars and van Krevelen redox mechanism. The studies employed the steady state isotopic transient kinetic analysis (SSITKA) technique which enables *in situ* measurements. The technique is very useful because it provides a lot of kinetic data about the reaction mechanism and the catalyst–surface reaction intermediates [23,24]. The method was devised by Happel, Bennett and Biloen and it is described in [23–25]. It consists in measuring (using mass spectrometer) the change of the isotopic composition of the substrates and products of the reaction which follows the substitution of one of the reactants with an isotopic-label reactant. The switch is executed in the steady state of the reaction proceeding on the catalyst surface and does not cause any change in its conditions. The temperature, pressure, flow, concentration of reactants and products of the reaction, both in the gas phase and adsorbed on the catalyst surface, do not undergo any change. The concentrations of all the intermediates on the catalyst surface also remain unchanged, which makes it possible to determine their real amounts and the average life-times on the surface of the ‘‘working’’ catalyst.

2. Experimental

The Pd/Al_2O_3 catalyst was obtained by using the so-called double impregnation of the Al_2O_3 support (Engelhard Al-0104). The first impregnation was performed in a 0.1 M EDTA solution at the temperature of 343 K (impregnation time: 30 min) and dried at 388 K (60 min). The second impregnation was performed in an acidic (pH 1.6) aqueous solution of 10 g of palladium nitrate in 1 dm^3 (impregnation time: 5 min). The precursor was then dried at 388 K (12 h) and calcined at 773 K (1 h). Prior to the use the catalysts were reduced with hydrogen at 873 K for 2 h.

The palladium content in the catalyst was determined by the X-ray fluorescence (XRF) method. Pellets for the XRF analysis were prepared by pressing catalysts powder. The measurements were performed by the energy-dispersive XRF spectrometer (Canberra 1510) equipped with the liquid nitrogen-cooled Si(Li) detector. The AXIL software package was used for spectral deconvolution and for the calculation of palladium content.

The total surface area of the palladium catalyst was determined by using the BET method, as a result of argon adsorption on the catalyst surface at liquid nitrogen (77 K) temperature, assuming that an argon atom occupies the surface of 0.157 nm^2. The measurements were carried out in the ASAP 2405N v1.0 analyser (Micromeritics).

The preliminary temperature-programmed experiments indicated that palladium oxide was reduced at a little higher temperature than the room temperature [26,27]. The decomposition of palladium hydride was observed at 340 K. At the temperature of 383 K palladium hydride was completely decomposed. Because of those findings hydrogen chemisorption at 383 K was measured in the Autosorb-1-C analyser (Quantachrome). The mean size of palladium crystallites ($d_{Pd} = 1.12/D_{Pd}$; D_{Pd} is palladium dispersion) were calculated on the basis of the total hydrogen chemisorption (H:Pd = 1:1) under equilibrium pressure of 13.3 kPa.

The characterization results of the Pd/Al_2O_3 catalyst were: palladium content 0.364 wt.%, total surface area 38.9 m^2/g, palladium dispersion 0.1686 and mean size of palladium crystallites 6.7 nm.

The mean size of palladium crystallites was confirmed by transmission electron microscopy (TEM)—LEO 906 operated at 120 eV. The sample for those measurements was prepared by placing droplets of a suspension of the catalyst in ethanol onto a standard Cu grid covered by a thin Formvar layer; then evaporating off the solvent in air at room temperature [28].

Since the palladium contents in the catalyst is rather low and because of the overlapping of diffraction lines of palladium and that of Al_2O_3 the precise determination of the crystallite size by the X-ray powder diffraction (XRD) method would be saddled with great errors, so only qualitative estimate, based on the shape of subtracted palladium peaks, was possible to get [27]. The XRD patterns were collected with an upgraded Zeiss HZG-4 diffractometer using Ni-filtered Cu Kα radiation. The sample was scanned by a step-by-step technique, at 2θ intervals of 0.05° and recording time of 10 s for each step. The measured patterns were compared with the JCPDS (Joint Committee on Powder Diffraction Standards) database for phase identification.

The activity of the catalyst was established on the basis of the measurements of the course of methane oxidation at various temperatures. The measuring apparatus consisted of the reactant-dosing system, ensuring the appropriate composition of the reaction mixture (2 vol.% of methane in air, and space velocity equal to 90,000 $cm^3/(g_{cat}\,h)$), the reaction system (a quartz reactor filled with the catalyst (0.2 g, 0.75–1.0 mm) mixed with pieces of quartz of 0.75–1.2 mm in diameter at the ratio of 1:10 and placed in a resistance-heated electric furnace), and the analytic system in the form of a gas chromatograph with a TCD detector and a CTR-1 column (Alltech). As a result of the research conducted, it was established that 10%, 50% and 90% methane conversions are obtained at 583 K, 653 K and 733 K, respectively. More details on the catalyst activity measurements can be found in the studies [26,27].

2.1. Measurements using the SSITKA method

The measurements were conducted with an apparatus consisting of the reactant-dosing system, the reaction system and the analytic system. A detailed description of the apparatus has been presented in Fig. 1. The reactant-dosing system was constructed in such a way as to enable us to obtain an appropriate reaction mixture and to perform a quick switch between isotopic labels. A quartz reactor with a thin bed of the catalyst resting on a layer of non-porous quartz, placed in a resistance-heated electric furnace, constituted the reaction system. The temperature of the catalyst was determined by using a temperature controller and its value was measured using

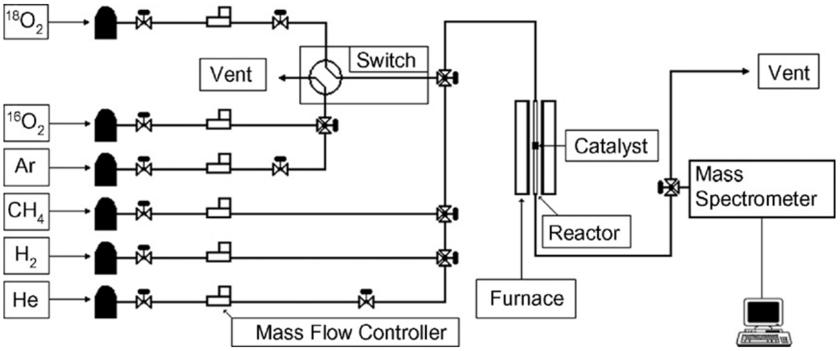

Fig. 1. The apparatus used in the SSITKA measurements.

a thermocouple placed inside the catalyst bed. The analytic system – the quadrupole mass spectrometer – which permitted an analysis of the reaction products, was connected to a computer collecting and processing measurement data.

The measurement was performed on 0.1 g of the catalyst (0.75–1.0 mm) in the reaction mixture containing 2% of methane, 6% of oxygen and helium as a balance. The $^{16}O_2$ isotope contained small admixture of argon, as an inert tracer of the hold-up of gases on their way from the valve switching between oxygen isotopes to the spectrometer's detector. The flow rate of the reaction mixture through the catalyst bed was 100 cm^3/min. The methane oxidation reaction was brought to the steady state at temperatures ensuring 10%, 50% and 90% of methane conversion and after the methane oxidation reaction had reached the steady state a switch was performed from $^{16}O_2/Ar/CH_4/He$ to $^{18}O_2/CH_4/He$.

2.2. The processing of measurement data obtained by means of the SSITKA method

The processing of measurement data obtained directly from the mass spectrometer was performed in several successive stages:

- the subtraction of the base line (the level of noises of the apparatus);
- the normalization of the concentration (the concentration of argon before the isotopic switch as well as the sum of concentrations of all oxygen isotopomers and all carbon dioxide isotopomers were assumed as an unity);
- the smoothing of the measurement points (at first Adjacent Averaging and next Fourier Transformate algorithms were used);
- the fitting of curves to the smoothed measurement points;
- the presentation of the results as changes of normalized concentrations of argon as well as oxygen and carbon dioxide isotopomers in the function of time after the isotopic switch;
- the determination of the average life-time of $^{16}O_2$ molecules released from the surface of the "working" palladium catalyst after switching from $^{16}O_2/Ar/CH_4/He$ to $^{18}O_2/CH_4/He$;
- the determination of the average life-time of intermediates leading to the formation of carbon dioxide, present on the surface of the "working" palladium catalyst after switching from $^{16}O_2/Ar/CH_4/He$ to $^{18}O_2/CH_4/He$;
- the calculation of the total number of $^{16}O_2$, $^{16}O^{18}O$ molecules, $N_{^{16}O_2}$ and $N_{^{16}O^{18}O}$, and intermediates leading to the formation of $C^{16}O_2$ and $C^{16}O^{18}O$, $N_{C^{16}O_2}$ and $N_{C^{16}O^{18}O}$ (counted per 1 g of the catalyst) present on the surface of the palladium catalyst in the course of the reaction. Values of $N_{^{16}O_2}$, $N_{^{16}O^{18}O}$, $N_{C^{16}O_2}$ and $N_{C^{16}O^{18}O}$ were calculated on the basis of real concentrations of $^{16}O_2$, $^{16}O^{18}O$, $C^{16}O_2$ and $C^{16}O^{18}O$, which were leaving the reactor.

3. Results and discussion

The results which were obtained for the reaction of methane oxidation on the Pd/Al_2O_3 catalyst by the SSITKA method at temperatures 583 K, 653 K and 733 K are shown as changes in normalized concentrations of oxygen ($^{16}O_2$, $^{16}O^{18}O$, $^{18}O_2$), carbon dioxide ($C^{16}O_2$, $C^{16}O^{18}O$, $C^{18}O_2$) and argon, in the function of the time after switching from $^{16}O_2/Ar/CH_4/He$ to $^{18}O_2/CH_4/He$ (Figs. 2–4). At all temperatures, after the oxygen isotopes switching, the concentrations of $^{16}O_2$, $C^{16}O_2$ and argon decrease, while the concentrations of $^{18}O_2$ and $C^{18}O_2$ increase and there appear certain amounts of oxygen and carbon dioxide molecules including two different isotopes ($^{16}O^{18}O$ and $C^{16}O^{18}O$). Moreover, delays are observed between the signal coming from $^{16}O_2$ and the signal coming from the argon tracer (argon—the inert gas which does not undergo adsorption on the catalyst surface at the temperature of methane oxidation) and also between the signal coming from $C^{16}O_2$ and the signal coming from the argon tracer. The delays between the signal coming from $^{16}O_2$ and the signal coming from the argon tracer indicate that a large amount of oxygen is retained on the catalyst surface, which is confirmed by calculating the number of $^{16}O_2$ present on the surface of the palladium catalyst $N_{^{16}O_2}$ after the switch between $^{16}O_2/Ar/CH_4/He$ and $^{18}O_2/CH_4/He$ (Table 1). The values of $N_{^{16}O_2}$ decrease as the temperature increases, which is also a consequence of increasing methane conversion (a larger amount of oxygen from the catalyst surface takes part in methane oxidation and there is less oxygen for desorption). The average life-time $\tau_{^{16}O_2}$ (Table 1) of oxygen molecules on the catalyst surface also decreases. The oxygen is retained on the catalyst surface more briefly, so the bonding strength of oxygen with the catalyst surface is weaken. The

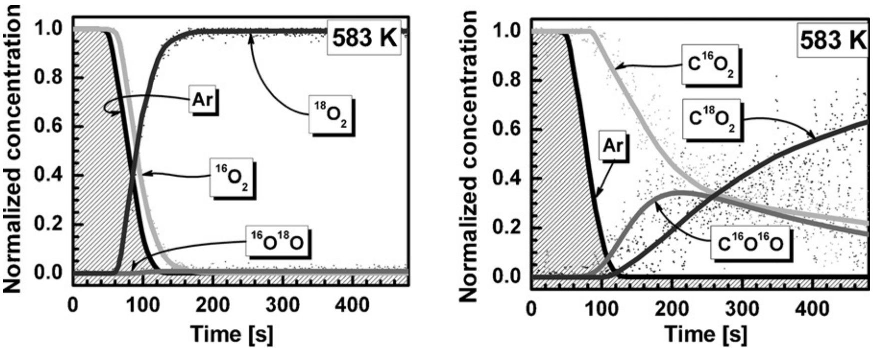

Fig. 2. The results of switching from $^{16}O_2/Ar/CH_4/He$ to $^{18}O_2/CH_4/He$ at the temperature of 583 K, ensuring 10% of methane conversion.

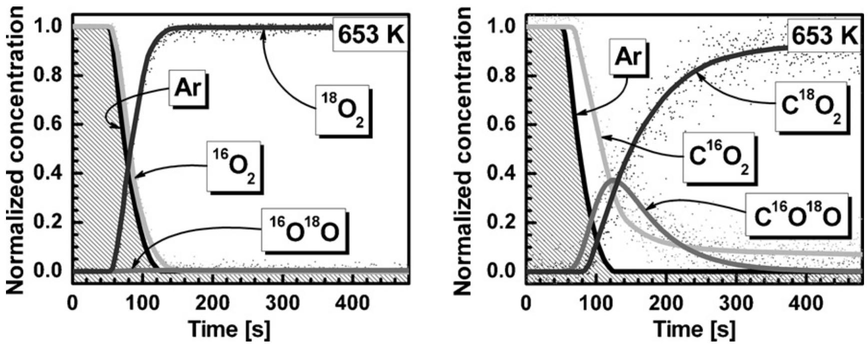

Fig. 3. The results of switching from $^{16}O_2/Ar/CH_4/He$ to $^{18}O_2/CH_4/He$ at the temperature of 653 K, ensuring 50% of methane conversion.

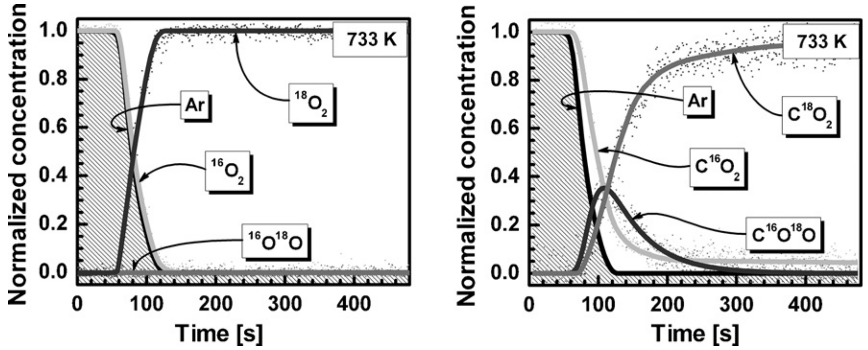

Fig. 4. The results of switching from $^{16}O_2/Ar/CH_4/He$ to $^{18}O_2/CH_4/He$ at the temperature of 733 K, ensuring 90% of methane conversion.

$^{16}O^{18}O$ which was produced after the switch of isotopes testifies to the proceeding of the exchange of oxygen from the gas phase with lattice ions O^{2-} of the Pd/Al_2O_3 catalyst. Moreover, the exchange between $^{16}O_2$ and $^{18}O_2$ in the gas phase was not possible, because in the reaction mixture which was used for the methane oxidation was present only one oxygen isotope (at first $^{16}O_2$ and after the switch $^{18}O_2$). The gas phase including $^{16}O_2$ was in the contact with the gas phase including $^{18}O_2$ only during the oxygen isotopes switching. The switching time in our experiments was very short. Potentially, the exchange of oxygen can occur both with O^{2-} ions of the active phase and with O^{2-} ions of the Al_2O_3 support. The exchange of oxygen from the gas phase with the lattice ions O^{2-} of the Al_2O_3 support begins above 723 K, which is confirmed by the investigations presented in [26,27] and so at lower temperatures it occurs only with the active phase. The presence of oxygen molecules including two different isotopes of oxygen which were obtained by the exchange of oxygen at 583 K indicates that PdO is present even at such a low temperature [27]. It proves that some part of the palladium phase, initially reduced directly before the reaction, is oxidized during the flameless combustion of methane. This is in the agreement with other studies [13–15], particularly with [12] which shows by operando Raman spectroscopy that the surface of palladium phase is in the intermediate state between surface lacunary PdO and crystalline PdO. Methane oxidation is not catalysed by Al_2O_3 at such a low temperature (583 K) and there is a faint possibility of oxygen transfer between the lattice of the support and the lattice of the active phase.

Figs. 2–4 also present the results obtained for the product of methane oxidation—carbon dioxide. As in the case of oxygen, also here significant delays are observed between the signal

Table 1
Results of the SSITKA experiments in the flameless combustion of methane over the Pd(PdO)/Al_2O_3 catalyst (on the 1 g of the catalyst basis)

Reaction temperature (K)	583	653	733
Methane conversion (%)	10	50	90
$N_{^{16}O_2} \times 10^{20}$	4.17	1.92	0.58
$N_{^{16}O^{18}O} \times 10^{20}$	0.59	0.30	0
$N_{C^{16}O_2} \times 10^{20}$	1.62	3.28	4.46
$N_{C^{16}O^{18}O} \times 10^{20}$	0.87	1.90	2.60
$\tau_{^{16}O_2}$ (s)	16.71	10.71	5.39
$\tau_{C^{16}O_2}$ (s)	180.35	73.19	45.22

$N_{^{16}O_2}$, $N_{^{16}O^{18}O}$—numbers of $^{16}O_2$ and $^{16}O^{18}O$ molecules present on the surface of the “working” palladium catalyst after switching from $^{16}O_2/Ar/CH_4/He$ to $^{18}O_2/CH_4/He$; $N_{C^{16}O_2}$, $N_{C^{16}O^{18}O}$—numbers of $C^{16}O_2$ and $C^{16}O^{18}O$ molecules, corresponding to the number of intermediates leading to the formation of carbon dioxide, present on the surface of the “working” palladium catalyst after switching from $^{16}O_2/Ar/CH_4/He$ to $^{18}O_2/CH_4/He$; $\tau_{^{16}O_2}$—the average life-time of $^{16}O_2$ molecules present on the surface of the “working” palladium catalyst after switching from $^{16}O_2/Ar/CH_4/He$ to $^{18}O_2/CH_4/He$; $\tau_{C^{16}O_2}$—the average life-time of intermediates leading to the formation of carbon dioxide, present on the surface of the “working” palladium catalyst after switching from $^{16}O_2/Ar/CH_4/He$ to $^{18}O_2/CH_4/He$.

coming from $C^{16}O_2$ and the signal coming from the inert tracer, argon. The delays between the signal coming from $C^{16}O_2$ and the signal coming from the argon tracer are considerably longer than those between the signal coming from $^{16}O_2$ and the signal coming from the argon tracer. The molecules of $C^{16}O_2$ remain in gases flowing out from the reactor even 8 min after the influx of $^{16}O_2$ to the reactor has been cut off. This suggests unambiguously that oxygen from the lattice of the catalyst must be taking part in methane oxidation and that the reaction proceeds according to the Mars and van Krevelen redox mechanism. Our results are consisted with some earlier literature reports [17,21,22], which suggested such a mechanism of methane oxidation. Additionally, this fact is proved by the presence of large amounts of carbon dioxide with two different oxygen isotopes $N_{^{16}O^{18}O}$ as well as the amount of $C^{16}O_2$ produced after the switch of isotopes. It is worth to notice that in the spite of similar values of $N_{C^{16}O^{18}O}$ and $N_{^{16}O^{18}O}$ at 583 K, their normalized concentrations in Fig. 2 are different. This is due to the higher concentration of dioxygen than that of carbon dioxide in the reactor effluent at that temperature. The amount of $C^{16}O_2$ produced after the switch of isotopes corresponds to the number of intermediates leading to the formation of carbon dioxide, $N_{C^{16}O_2}$, and present on the catalyst surface during methane oxidation. The participation of oxygen from the lattice of the catalyst in methane oxidation is also indicated by the long average life-time of intermediates leading to the formation of carbon dioxide $\tau_{C^{16}O_2}$, present on the catalyst surface (Table 1). $N_{C^{16}O_2}$ and $\tau_{C^{16}O_2}$ reach very high values, which proves that a large amount of $C^{16}O_2$ has been formed out of the oxygen from the lattice of the catalyst after the switch of isotopes. With the increase of the reaction temperature, after switching of isotopes, larger amounts of $C^{16}O_2$ and $C^{16}O^{16}O$ ($N_{C^{16}O_2}$ and $N_{C^{16}O^{18}O}$ are increasing) are observed, which indicates that there is an increase in the number of active centres on the catalyst surface—a larger amount of oxygen from the lattice of the catalyst is accessible for the reaction of methane oxidation. The changes in the real number of active centres with the reaction temperature should be taken into account in the determination of the turnover number values. This is an important contribution of our results to the knowledge on the methane oxidation kinetics. The calculated values of the average life-time of intermediates leading to the formation of carbon dioxide, present on the catalyst surface ($\tau_{C^{16}O_2}$), decrease as the reaction temperature increases. This is compatible with the assumptions presented by Shannon et al. [23], that if a reaction is of a first or pseudo-first order then the rate constant is the inverse of the average surface life-time. The flameless combustion of methane on the palladium catalyst is the pseudo-first order, what confirms earlier literature report [29].

On the basis of average surface life-times of intermediates leading to the formation of carbon dioxide $\tau_{C^{16}O_2}$ the rate constant and the activation energy of the reaction of methane oxidation were calculated. However, the value of the activation energy was about 24 kJ/mol what is much lower than 80 kJ/mol which is typically reported in literatures [30,31]. That difference may be caused by two reasons. One of them—the values of the $\tau_{C^{16}O_2}$ $\tau_{C^{16}O_2}$ are overstated because in the oxidation of methane oxygen from the lattice of palladium catalyst takes part. The another reason for much lower value of the activation energy calculated from our results are high methane conversions, up to 90%. The acceptable values of the activation energy may be obtained only at low conversions at which mass and heat transfer limitations are neglected.

There is still an open question what is/are the surface intermediate(s) leading to the formation of carbon dioxide. The SSITKA experiments do not provide any indications on the kind of adsorbed species. Demoulin et al. [13] on the basis of their in situ and operando DRIFTS experiments have found no methane-adsorbed species on the Pd/Al_2O_3 catalyst under reaction conditions. Formates/carbonates are transient species that disappear when the reaction of methane oxidation begins and they were considered only as a true spectator species. Under standard oxygen-rich conditions the Pd^0–CO species were also not observed; CO was oxidized very quickly. However, in our opinion, CO as well as carbide species could be considered as surface intermediates in the oxidation of methane over the Pd(PdO)/Al_2O_3 catalyst. We hope that the SSITKA studies with $^{12}CH_4$ and $^{13}CH_4$ will be useful for enrichment of the knowledge on the mechanism of the catalytic oxidation of methane.

4. Conclusions

The results obtained by the SSITKA method concerning methane oxidation over the palladium catalyst prove that the oxygen from the lattice of the catalyst takes part in this process. This suggests that the reaction proceeds according to the Mars and van Krevelen redox mechanism. The oxidation of palladium to palladium oxide in the course of flameless methane combustion occurs even at 583 K. With the increase of the reaction temperature there is an increase in the number of active centres on the Pd(PdO)/Al_2O_3 catalyst surface—a larger amount of oxygen from the lattice of the catalyst is accessible for the reaction of methane oxidation. The changes in the real number of active centres with the reaction temperature should be taken into account in the determination of the turnover number values. Parallel to the process of methane oxidation, the exchange of oxygen occurs between the gas phase and lattice ions O^{2-} of the catalyst. This is confirmed by the presence of $^{16}O^{16}O$ molecules after the isotopic switch from $^{16}O_2/Ar/CH_4/He$ to $^{18}O_2/CH_4/He$, at the same time proving that a considerable amount of the palladium was oxidized to palladium oxide. The participation of lattice ions O^{2-} of the catalyst in methane oxidation intensifies along with the rising temperature, which is related, among other things, to the increase of the amount of palladium oxide in the catalyst.

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