

# 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<sub>2</sub>O<sub>3</sub> catalyst by using the steady state isotopic transient kinetic analysis method. During the reaction switches between <sup>16</sup>O<sub>2</sub>/Ar/CH<sub>4</sub>/He and <sup>18</sup>O<sub>2</sub>/CH<sub>4</sub>/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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> catalyst surface—a larger amount of oxygen from the lattice of the catalyst is accessible for the reaction of methane oxidation.

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## 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<sub>2</sub>O<sub>3</sub> 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<sub>2</sub>O<sub>3</sub> catalyst was obtained by using the so-called double impregnation of the Al<sub>2</sub>O<sub>3</sub> 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<sup>3</sup> (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<sup>2</sup>. 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<sub>2</sub>O<sub>3</sub> catalyst were: palladium content 0.364 wt.%, total surface area 38.9 m<sup>2</sup>/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<sub>2</sub>O<sub>3</sub> 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 K $\alpha$  radiation. The sample was scanned by a step-by-step technique, at 2 $\theta$  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<sup>3</sup>/(g<sub>cat</sub> 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

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