Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2021, **31**, 635–637

Mendeleev Communications

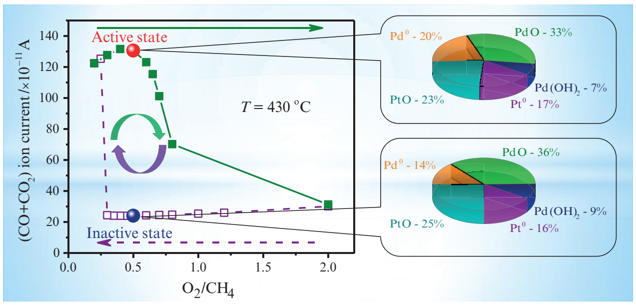
Investigation of concentration hysteresis in methane oxidation on bimetallic Pt–Pd/Al_2O_3 catalyst by *in situ* XPS and mass spectrometry

Igor A. Chetyrin,* Andrey V. Bukhtiyarov, Igor P. Prosvirin and Valerii I. Bukhtiyarov

G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. E-mail: chia@catalysis.ru

DOI: 10.1016/j.mencom.2021.09.014

A combination of *in situ* XPS and mass spectrometry was used to investigate concentration hysteresis in the low-temperature oxidation of methane over a bimetallic Pt–Pd catalyst. It was shown that a decrease in the oxygen concentration leads to a sharp increase in the catalytic activity of the sample under study. The transition of the catalyst to a high/low activity state occurs due to the partial reduction/oxidation of the active component, with both platinum and palladium participating in the methane oxidation reaction.



Keywords: concentration hysteresis, methane, oxidation, platinum, palladium, bimetallic catalysts, *in situ* XPS, mass spectrometry.

For the first time, we recently observed concentration hysteresis in low-temperature oxidation of methane over nanosized platinum particles supported on γ-Al_2O_3, with a reversible change in the O_2/CH_4 ratio from lean to rich conditions.[1,2] The catalytic system exhibited low and high activity under the same external conditions, depending on the direction of changing the O_2/CH_4 ratio. The catalyst transition to the active state occurred at O_2/CH_4 ratio close to 1 when O_2 concentration in the reaction mixture diminishes and was accompanied by a significant increase in the methane oxidation rate and appearance of H_2 and CO in the reaction products. A reverse increase in the O_2 concentration in the reaction mixture to the O_2/CH_4 molar ratio > 2 resulted in an augmentation in the methane conversion. Then the system returned to its initial low-activity state when only CO_2 and H_2O were observed among the reaction products.[1] Such transitions can be repeated many times during the O_2/CH_4 ratio variation in the reaction mixture flow. It should also be noted that the theoretical prediction of the existence of concentration hysteresis in the oxidation of methane on Pt was made earlier by Zhdanov *et al.*[3] The authors presented a general model for the oxidation of CH_4 on Pt, emphasizing the role of the formation of surface oxides, which is interpreted within the framework of the theory of first-order phase transitions. It was shown by the Monte Carlo method that the formation of a surface oxide could lead to stepwise features of the reaction kinetics. In particular, with increasing CH_4 pressure, decreasing O_2 pressure, or both, the model predicts an abrupt transition from a low-activity state, when the surface is completely covered with oxide, to a high-activity state, when the surface is covered with chemisorbed oxygen. In the low-activity state, the reaction is first order in CH_4 and zero order in O_2. In a high-activity state, both orders of reaction are positive.

A detailed study of the system using X-ray absorption spectroscopy (both EXAFS and XANES) led us to conclude that the transition of supported platinum to the active state is caused by the partial reduction of oxidized platinum species under fuel-rich conditions. In contrast, partial oxidation of the platinum surface occurs during catalyst deactivation when the proportion of O_2 in the reaction mixture increases.[2]

A similar effect, namely concentration hysteresis, was reported by Bugosh *et al.*[4] for methane oxidation on bimetallic Pt–Pd catalysts. The authors suggested that the branch corresponding to the low conversion can be explained by inhibition due to the adsorption of O_2 occupying the metal catalyst sites. On the other hand, the stable branch corresponding to the high conversion is due to the supply of oxygen from the underlying bulk of PdO, which favors the partial oxidation of methane. However, it should be noted that the data of physicochemical methods did not confirm these assumptions.

A study of the system by *in situ* X-ray photoelectron spectroscopy (XPS) can shed some light on this topic. Indeed, we used *in situ* XPS to study concentration hysteresis in methane oxidation on monometallic Pt/γ-Al_2O_3 catalysts.[5,6] Even under conditions for *in situ* XPS measurements (submillibar pressure range of the reaction mixture *versus* atmospheric pressure in the measurements of catalysis), two stable stationary states with low and high catalytic activity were observed depending on the direction of change in the oxygen concentration in the reaction mixture.[5,6]

Thus, the aim of this work is to verify the existence of concentration hysteresis in the methane oxidation on a bimetallic Pd–Pt/Al_2O_3 catalyst, as well as to establish the relationship between the chemical state of catalyst surface and catalytic properties of the test sample depending on the reaction conditions, namely, during the implementation of concentration hysteresis. In this study, we used a Pd–Pt/Al_2O_3 catalyst (PdPt18) with palladium and platinum contents of 0.63 and 0.18 wt%, respectively, which exhibited the highest activity in methane oxidation due to synergistic effects.[7]

At the first stage, using mass spectrometry (MS), this bimetallic PdPt18 catalyst was tested in the methane oxidation at various ratios of methane and oxygen (the CH_4 pressure remained constant at 0.008 mbar, and the O_2 pressure varied) and various temperatures (430–460 °C). The purpose of the temperature variation experiments was to determine the effect of temperature on the hysteresis loop and verify the reproducibility of this phenomenon. The sum of the MS signals from CO and CO_2 was used to estimate catalytic activity in methane oxidation. As a result of the experiments, the boundaries of the existence of hysteresis were determined, which allowed us to select points for further measurements of the XPS spectra.

Figure 1 shows that a decrease in the oxygen concentration in the reaction mixture to some value of the O_2/CH_4 ratio causes a sharp activation of the initially inactive catalyst. The activity increases by about six times compared with the inactive state at 430 °C and about ten times at 460 °C. The reverse increase in the proportion of oxygen in the reaction mixture keeps the catalyst active so that catalytic activity has different levels at the same composition of the reaction mixture up to some critical value of the O_2/CH_4 ratio when the catalyst again goes into a low activity state. The presence of branches with low and high activity indicates the existence of concentration hysteresis. The reaction proceeds mainly along the path of complete oxidation; selectivity is about 80% for the active state and about 60% for the inactive state [Figure 1(*b*)].

It can also be seen that an increase in the sample temperature from 430 to 460 °C shifts the hysteresis loop for the bimetallic Pt–Pd catalyst towards higher values of the O_2/CH_4 ratio and narrows the loop width from about 0.3 to 0.2. Subsequent reverse cooling to a temperature of 430 °C leads to the return of the hysteresis loop to its initial state (activation point at O_2/CH_4 ratio = 0.25, hysteresis width 0.3). This temperature dependence of the hysteresis width is in good agreement with the previous results for monometallic Pt/Al_2O_3 catalysts.[1,2] Similar behavior was shown for Pt/Al_2O_3 catalysts,[5,6] but in the case of monometallic Pt catalysts, the hysteresis loop was narrower (0.1 *versus* 0.2) under the same reaction conditions [$P(CH_4)$ = 0.008 mbar, T = 460 °C] and was biased towards lower values of the O_2/CH_4 ratio.

Further, during the experiments, *in situ* XPS spectra were measured at the same O_2/CH_4 ratio of 1/2, both in the active [Figure 1(*a*), red point] and inactive [Figure 1(*a*), blue point] hysteresis states. Reference XPS spectra were also measured at the O_2/CH_4 ratio of 5/1, *i.e.*, for a completely deactivated catalyst. Figure 2 shows both the original spectra and the results of their deconvolution into individual components. Several peaks of platinum and palladium species with different binding energies are observed. The assignment of peaks to different chemical states of Pt and Pd was done based on our previous results[7] and published data.[8–24] Thus, the Pt $4f_{7/2}$ peak at ~71.1 eV and the Pd $3d_{5/2}$ peak at ~335.1 eV correspond to metallic platinum and palladium, respectively. The states with binding energies of 72.2 and 336.3 eV in the Pt $4f_{7/2}$ and Pd $3d_{5/2}$ spectra are attributed to the 2+ states in PtO and PdO, respectively. Finally, the peak with the highest Pd $3d_{5/2}$ binding energy of ~338.4 eV is assigned to the 2+ state of palladium in $Pd(OH)_2$.

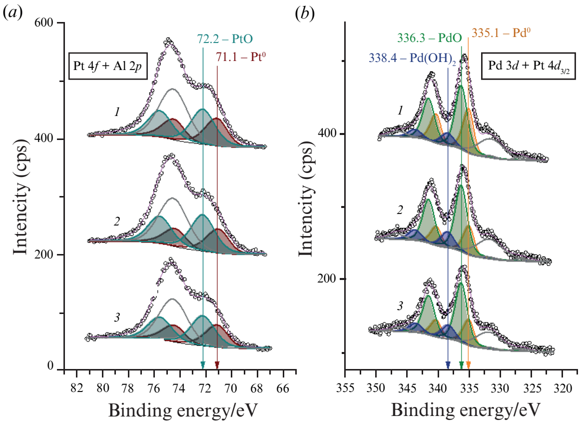


Figure 2 XPS spectra of (*a*) Pt 4*f* and (*b*) Pd 3*d* regions with line deconvolution, recorded for the bimetallic PdPt18 catalyst in the (*1*) active and (*2*),(*3*) inactive hysteresis states at the O_2/CH_4 ratio of (*1*),(*2*) 1/2 and (*3*) 5/1 and T = 430 °C.

Figure 3 shows the quantitative data of deconvolution, namely, the proportions of different species of platinum and palladium in the inactive (both initial and during hysteresis) and active states of the catalysts. These data show that a mixture of metallic and oxide species is required for the methane oxidation reaction to proceed in both active and inactive states of concentration hysteresis, and there is an optimal metal/oxide ratio to achieve the higher catalytic activity. A detailed analysis of the data presented in Figure 3 shows that both inactive states are characterized by a similar proportion of different palladium species, while the transition to active hysteresis states increases the ratio of palladium metal to oxide (2+) components from 0.39 to 0.61. Contrary to this, the corresponding ratio for Pt_{met} and Pt^{2+} species remains almost constant. In addition, we should note that the active state of the catalyst is characterized by a slight decrease in the concentration of $Pd(OH)_2$ species, which are well known to deactivate Pd catalysts for methane oxidation.

These data suggest that it is palladium that is responsible for the active state of the catalyst due to the partial reduction of PdO

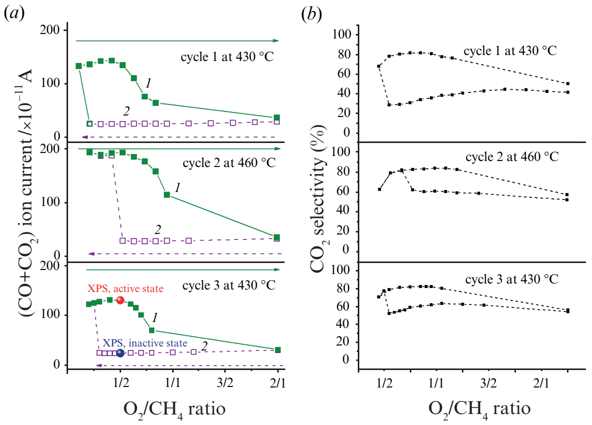


Figure 1 (*a*) Typical concentration hysteresis loops in methane oxidation on the PdPt18 catalyst: (*1*) a high activity branch and (*2*) a low activity branch. (*b*) Dependence of the CO_2 selectivity on the O_2/CH_4 ratio. Conditions: T = 430–460 °C, $P(CH_4)$ = 0.008 mbar and $P(O_2)$ = 0.004–0.016 mbar.

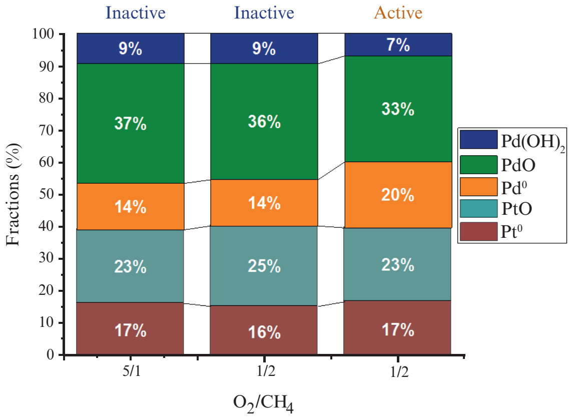


Figure 3 The fractions of different species of Pt and Pd for inactive and active hysteresis states according to *in situ* XPS data at T = 430 °C.

and $Pd(OH)_2$ to metallic palladium. This assumption is consistent with our recent data showing that monometallic palladium catalyst exhibits higher activity than the monometallic platinum catalyst.[7] Unfortunately, the role of platinum is still not fully understood and requires additional experiments, for example, using synchrotron radiation to perform depth profiling analysis. Apparently, platinum acts as a stabilizing additive and also takes part in the reaction, but to a lesser extent than palladium.

In conclusion, concentration hysteresis in methane oxidation on the bimetallic $Pd_{0.63}$–$Pt_{0.18}/Al_2O_3$ catalyst was observed in the submillibar pressure range (~0.01 mbar). These conditions allow us to use *in situ* XPS to study the chemical state of the catalyst during its transition from an inactive to an active state. The transition between high/low activity states is caused by the partial reduction/oxidation of palladium, while no change in the chemical state of platinum is observed. A mixture of the metallic and oxide states of Pd (and Pt) is required to achieve the best catalytic activity.

This work was performed within the framework of the budget project for the G. K. Boreskov Institute of Catalysis. The studies were conducted using the equipment of the Center of Collective Use ‘National Center of Catalyst Research’ at the G. K. Boreskov Institute of Catalysis.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.09.014.

References

1 I. Yu. Pakharukov, I. E. Bekk, M. M. Matrosova, V. I. Bukhtiyarov and V. N. Parmon, *Dokl. Phys. Chem.*, 2011, **439**, 131 (*Dokl. Akad. Nauk*, 2011, **439**, 211).

2 I. Yu. Pakharukov, A. Yu. Stakheev, I. E. Beck, Ya. V. Zubavichus, V. Yu. Murzin, V. N. Parmon and V. I. Bukhtiyarov, *ACS Catal.*, 2015, **5**, 2795.

3 V. P. Zhdanov, P.-A. Carlsson and B. Kasemo, *J. Chem. Phys.*, 2007, **126**, 234705.

4 G. S. Bugosh, V. G. Easterling, I. A. Rusakova and M. P. Harold, *Appl. Catal., B*, 2015, **165**, 68.

5 I. Yu. Pakharukov, I. P. Prosvirin, I. A. Chetyrin, V. I. Bukhtiyarov and V. N. Parmon, *Catal. Today*, 2016, **278**, 135.

6 I. A. Chetyrin, I. P. Prosvirin, I. Yu. Pakharukov and V. I. Bukhtiyarov, *Chem. Sustainable Dev.*, 2017, **25**, 91.

7 I. A. Chetyrin, A. V. Bukhtiyarov, I. P. Prosvirin, A. K. Khudorozhkov and V. I. Bukhtiyarov, *Top. Catal.*, 2020, **63**, 66.

8 A. K. Khudorozhkov, I. A. Chetyrin, A. V. Bukhtiyarov, I. P. Prosvirin and V. I. Bukhtiyarov, *Top. Catal.*, 2017, **60**, 190.

9 D. Zemlyanov, B. Aszalos-Kiss, E. Kleimenov, D. Teschner, S. Zafeiratos, M. Hävecker, A. Knop-Gericke, R. Schlögl, H. Gabasch, W. Unterberger, K. Hayek and B. Klötzer, *Surf. Sci.*, 2006, **600**, 983.

10 J. R. Croy, S. Mostafa, L. Hickman, H. Heinrich and B. Roldan Cuenya, *Appl. Catal., A*, 2008, **350**, 207.

11 S. Oh, S. Back, W. H. Doh, S. Y. Moon, J. Kim, Y. Jung and J. Y. Park, *RSC Adv.*, 2017, **7**, 45003.

12 X. Fan, F. Wang, T. Zhu and H. He, *J. Environ. Sci.*, 2012, **24**, 507.

13 H.-P. Steinrück, F. Pesty, L. Zhang and T. E. Madey, *Phys. Rev. B*, 1995, **51,** 2427.

14 K. Otto, L. P. Haack and J. E. deVries, *Appl. Catal., B*, 1992, **1**, 1.

15 T. L. Barr, *J. Phys. Chem.*, 1978, **82**, 1801.

16 R. S. Monteiro, D. Zemlyanov, J. M. Storey and F. H. Ribeiro, *J. Catal.*, 2001, **201**, 37.

17 K. Sun, W. Lu, M. Wang and X. Xu, *Appl. Catal., A*, 2004, **268**, 107.

18 G. M. Bancroft, I. Adams, L. L. Coatsworth, C. D. Bennewitz, J. D. Brown and W. D. Westwood, *Anal. Chem.*, 1975, **47**, 586.

19 E. A. Anumol, A. Halder, C. Nethravathi, B. Viswanath and N. Ravishankar, *J. Mater. Chem.*, 2011, **21**, 8721.

20 S. A. Yashnik, Yu. A. Chesalov, A. V. Ishchenko, V. V. Kaichev and Z. R. Ismagilov, *Appl. Catal., B*, 2017, **204**, 89.

21 A. Large, J. Seymour, W. Quevedo Garzon, K. Roy, F. Venturini, D. C. Grinter, L. Artiglia, E. Brooke, M. Briceno de Gutierrez, A. Raj, K. R. J. Lovelock, R. A. Bennett, T. Eralp-Erden and G. Held, *J. Phys. D: Appl. Phys.*, 2021, **54**, 174006.

22 R. Price, T. Eralp-Erden, E. Crumlin, S. Rani, S. Garcia, R. Smith, L. Deacon, C. Euaruksakul and G. Held, *Top. Catal.*, 2016, **59**, 516.

23 R. Arrigo, M. E. Schuster, Z. Xie, Y. Yi, G. Wowsnick, L. L. Sun, K. E. Hermann, M. Friedrich, P. Kast, M. Hävecker, A. Knop-Gericke and R. Schlögl, *ACS Catal.*, 2015, **5**, 2740.

24 H. Gabasch, K. Hayek, B. Klötzer, W. Unterberger, E. Kleimenov, D. Teschner, S. Zafeiratos, M. Hävecker, A. Knop-Gericke, R. Schlögl, B. Aszalos-Kiss and D. Zemlyanov, *J. Phys. Chem. C*, 2007, **111**, 7957.

Received: 22nd March 2021; Com. 21/6499