

# Oxidation of propylene over Pd(551): Temperature hysteresis induced by carbon deposition and oxygen adsorption

Andrey V. Matveev<sup>a,\*</sup>, Vasily V. Kaichev<sup>a,b</sup>, Andrey A. Saraev<sup>a</sup>, Vladimir V. Gorodetskii<sup>a</sup>,  
Axel Knop-Gericke<sup>c</sup>, Valerii I. Bukhtiyarov<sup>a,b</sup>, Bernard E. Nieuwenhuys<sup>d</sup>

<sup>a</sup> *Boriskov Institute of Catalysis of the Siberian Branch of the Russian Academy of Science, Pr. Acad. Lavrentieva 5, 630090, Novosibirsk, Russia*

<sup>b</sup> *Novosibirsk State University, Pirogova St. 2, 630090, Novosibirsk, Russia*

<sup>c</sup> *Department of Inorganic Chemistry, Fritz Haber Institute of the Max Plank Society, Faradayweg 4-6, D-14195 Berlin, Germany*

<sup>d</sup> *Leiden Institute of Chemistry, Leiden University, P.O. Box 9502, Einsteinweg 55, 2333 CC Leiden, the Netherlands*

## A B S T R A C T

The oxidation of propylene over a Pd(551) single crystal surface has been studied by X-ray photoelectron spectroscopy (XPS) and temperature-programmed reaction spectroscopy during both heating and cooling in various oxygen/propylene mixtures. In all the experiments, the partial pressure of propylene was approximately  $1 \times 10^{-7}$  mbar and the partial pressure of oxygen was varied to achieve molar oxygen/propylene ratios of 1, 3, 10, and 100. Under all these conditions, we observed a temperature hysteresis: temperature dependences of the catalyst activity and product distribution were different during heating and cooling. It was shown that the temperature hysteresis was due to concurrent accumulation of carbon and oxygen atoms on the palladium surface. At low temperatures, a high concentration of carbonaceous deposits detected by XPS resulted in a low catalytic activity due to blocking of the palladium surface. Increasing temperature led to full dehydrogenation of the carbonaceous species and dissolution of carbon atoms into subsurface palladium layers. As a result, even under oxygen-rich conditions, the formation of a PdC<sub>x</sub> phase was detected by XPS at 373 K. This process had no influence on the selectivity in the oxidation of propylene at least under UHV conditions. A shift of selectivity toward CO<sub>2</sub> was found to result from an increase in the oxygen concentration on the palladium surface. The state with a low catalytic activity in the oxidation of propylene was associated with palladium in the metallic state covered by carbon deposits. The high-active state of palladium was associated with palladium in the metallic state with a high concentration of chemisorbed oxygen and a moderate concentration of a surface oxide. Bulk PdO was not detected by XPS under all conditions used.

---

\* Corresponding author. Tel.: +7 (383) 3306732; fax: +7 (383) 3308356.

E-mail address: matveev@catalysis.ru (A.V. Matveev).

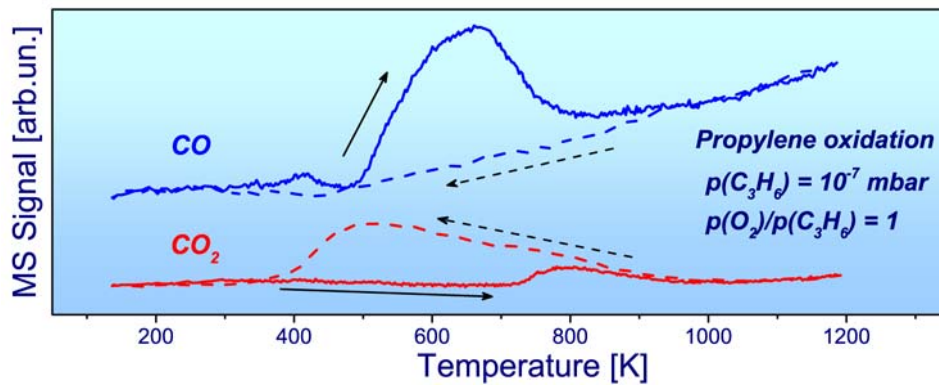
*Keywords:*

Heterogeneous catalysis

Palladium

Propylene oxidation

Temperature hysteresis



### Highlights

The oxidation of propylene over Pd(551) has been studied by XPS and TPRS under UHV.

A temperature hysteresis in activity and selectivity has been found.

The hysteresis is caused by a concurrent accumulation of carbon and oxygen on Pd.

## 1. Introduction

Palladium is used in various catalytic applications because of its high intrinsic activity and its relatively low price compared with other noble metals. In particular, Pd-based catalysts are used for the purification of automotive exhaust gases that contain significant amounts of unburned fuel and other hydrocarbons formed by pyrolysis [1-3]. Many studies have been devoted to the combustion of hydrocarbons over Pd-based catalysts [4-6]. However, the mechanism for the oxidation of hydrocarbons over palladium is still not fully understood. The mechanism is complex and the catalyst activity and selectivity are influenced by variations in the process pressure, temperature, and the gas mixture composition. Moreover, under oxidizing conditions, Pd-based catalysts can exhibit an interesting dynamic behavior, including hysteresis phenomena, self-sustained rate oscillations, spatial pattern formation, and deterministic chaos; a fast deactivation of palladium is frequently observed as well [7-18]. It is obvious that in all these cases a change in the chemical state of palladium determines the catalytic performance, causing the critical phenomena or catalyst deactivation. To develop more-effective Pd-based catalysts with a high activity in a wide temperature range, the reasons that cause these phenomena have to be understood.

The main objective of this work was to study the oxidation of propylene over palladium in a wide range of temperatures and pressures under which the temperature hysteresis is observed. It allowed us to clarify the mechanism for deactivation of palladium during the combustion of hydrocarbons and the influence of the chemical state of palladium on its activity and product distribution. Propylene was chosen as a model hydrocarbon because it is a light unsaturated hydrocarbon, which is typically detected in automotive exhaust gases at a considerable concentration. The reasons for the decrease or increase in activity of palladium were unraveled by X-ray photoelectron spectroscopy (XPS) and temperature-programmed reaction spectroscopy (TPRS). XPS is one of the powerful tools in the catalytic surface science to investigate both the surface composition and the nature of adsorbed species; while TPRS can provide direct information about catalytic properties of samples under study [19-22]. A Pd(551) single crystal was used as a model catalyst. Because the stepped surface of Pd(551) consists of many regular defects (the surface contains three-atomic terraces of the (110) plane separated by the (111) steps), it is a good model for the surface of metal nanoparticles in supported catalysts. It is generally accepted that stepped surface of metal nanoparticles plays an important role in their catalytic activity [23].

## 2. Experimental

The TPRS measurements were performed in an ultra-high vacuum (UHV) surface analysis system at the Leiden Institute of Chemistry (Leiden University, Leiden, the Netherlands). The

system was equipped with facilities for Ar<sup>+</sup> ion sputtering, low energy electron diffraction (LEED), Auger electron spectroscopy (AES) and a shielded, differentially pumped, UTI-400 quadrupole mass-spectrometer (MS). The system was continuously pumped by turbomolecular pumps backed by mechanical pumps and the base pressure before each experiment was better than  $3 \times 10^{-10}$  mbar. The Pd sample was a disk (diameter 6 mm, thickness 1 mm) cut to within  $0.1^\circ$  of the {551} plane. The sample was mounted by means of two W wires spot-welded to the crystal edges, allowing the sample to be resistively heated from 120 to 1300 K. A K-type thermocouple was also spot-welded to the crystal rear to monitor the temperature. A typical heating/cooling rate was 1 K/s. Before each TPRS experiment, the sample was cleaned by repeated cycles of Ar-ion sputtering (3 keV, 1  $\mu$ A) at 300 K for 30 min, followed by an oxygen treatment (1000 K,  $10^{-7}$  mbar O<sub>2</sub>) for 20 min to remove carbon and subsequent annealing in vacuum for 5 min at 1200 K to remove oxygen. The structure and cleanliness of the surface of the single crystal were checked by AES and LEED. For the TPRS measurements, the sample was brought into close proximity of a 2-mm aperture of a MS nozzle to reduce the contribution from the heating wires and the edges of the single crystal. Six MS signals with m/z ratios of 2 (H<sub>2</sub>), 18 (H<sub>2</sub>O), 28 (CO), 32 (O<sub>2</sub>), 41 (the most intense fragment of C<sub>3</sub>H<sub>6</sub>), and 44 (CO<sub>2</sub>) were monitored simultaneously without correction to sensitivity factors. Note that the intensity of a MS signal of propylene with m/z = 28 is about 2.5 % of the main signal (m/z = 41), therefore a contribution of this signal to the CO signal was insignificant. Gases of high purity (O<sub>2</sub>: 99.998 %, C<sub>3</sub>H<sub>6</sub>: 99.99 %) were used without further purification. The flow rates of O<sub>2</sub> and C<sub>3</sub>H<sub>6</sub> were regulated separately with leak-valves.

The XPS experiments were carried out at the synchrotron radiation facility, BESSY II (Berlin, Germany) using the ISSS (Innovative Station for *In Situ* Spectroscopy) beamline. The experimental station was described in detail elsewhere [20]. Its key feature is a differentially pumped electrostatic lens system of a hemispherical analyzer, which allows analysis of the sample in the low mbar pressure region. The same Pd(551) single crystal was used in these experiments. The crystal was mounted on a sapphire sample holder between a SiC plate and a stainless steel plate, which had a hole of 5 mm in diameter. The sample was heated from the rear through the SiC plate with a near-infrared semiconductor laser ( $\lambda = 808$  nm). The sample temperature was measured with a K-type thermocouple spot-welded to the crystal edge.

Before each experiment, the single crystal was cleaned using the procedure described above. After cooling to room temperature, a flow of oxygen was set to provide a partial pressure approximately  $1 \times 10^{-7}$  mbar and then a flow of propylene was set to achieve a molar oxygen/propylene ratio 1:1. Other molar ratios were set by increasing the flow of oxygen. The flows of reactants were also regulated separately with leak-valves. Before XPS measurements, a heating/cooling cycle with a rate  $\pm 1$  K/s was carried out. The *C1s*, *O1s*, and *Pd3d* core-level spectra

were measured *in situ* with a photon energy of 720 eV. Photoelectrons were collected in the normal direction with respect to the sample surface. The spectra were normalized by the ring current. Curve fitting was done by the CasaXPS software. The line-shape used in the fit of the *C1s* and *O1s* spectra was the product of Lorentzian and Gaussian functions. An asymmetric so-called “LF line-shape” was used for approximation of different components in the  $\text{Pd}3d_{5/2}$  spectra. It is important to note that the asymptotic form of the LF line-shape is equivalent to the asymptotic form of the theoretical Doniach-Sunjc asymmetric line-shape. However, this new line-shape describes the asymmetric XPS peak more correctly than a conventional Doniach-Sunjc function does because the LF function is finite. A Shirley-type background was subtracted in all these cases.

### 3. Results and discussion

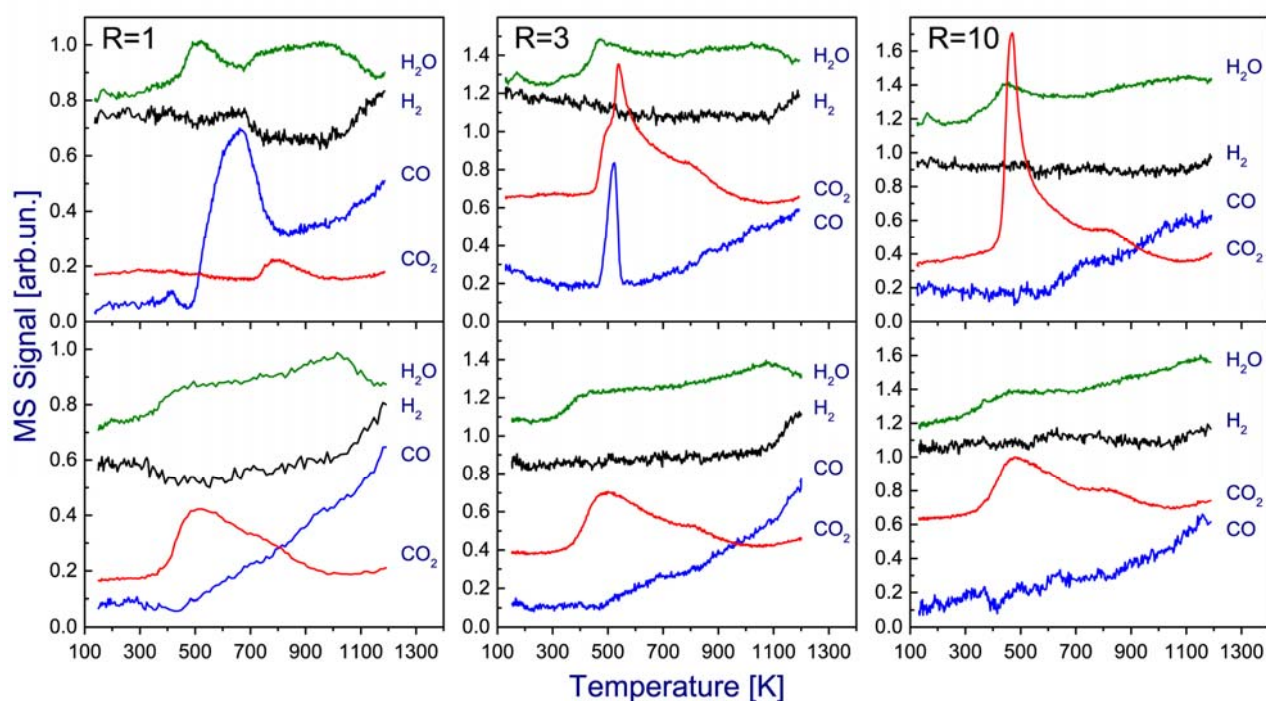
Two sets of experiments were performed. The first set was a series of TPRS experiments with the mass-spectrometric analysis of the gas phase during heating and cooling of the Pd(551) single crystal with a constant rate between 120 and 1200 K. The second set was measurements of the *C1s*, *O1s*, and  $\text{Pd}3d$  core-level spectra of the palladium surface at 373, 523, 673, and 773 K during stepwise heating from room temperature and subsequent cooling in the same manner. The spectra were acquired at the set temperature for approximately 30 minutes; the heating/cooling rate between the XPS measurements was 1 K/s. In both cases, the partial pressure of propylene was approximately  $1 \times 10^{-7}$  mbar in all the experiments, while the partial pressure of oxygen was varied to achieve molar oxygen/propylene ratios (R) of 1, 3, 10, and 100. To diminish the role of prehistory of the palladium surface in the TPRS experiments, the sample was heated in a flow of the reaction mixture, then cooled and heated again. It was shown that the surface prehistory was not significant; however, the data obtained during the first heating were not analyzed.

It was found that a temperature hysteresis exists under all these conditions: a temperature dependence of the product distribution during heating differed from that during cooling. Fig. 1 displays the TPRS profiles obtained during heating and cooling Pd(551) in the reaction mixtures with the molar oxygen/propylene ratios R equal to 1, 3, and 10. One can see that the TPRS profiles on the heating branch strongly depend on the oxygen content, whereas all the TPRS profiles on the cooling branch look similar. Under oxygen-lean conditions (R = 1), the dominant reaction product during the heating ramp was CO, while  $\text{CO}_2$  formation was negligible. The CO formation started at  $\sim 470$  K, passed through a maximum at  $\sim 660$  K, then decreased to reach a minimum at  $\sim 830$  K, and then slowly increased with temperature. The  $\text{CO}_2$  formation started at  $\sim 710$  K and passed through a maximum at  $\sim 790$  K. Water appeared as a peak with a maximum at 510 K and as a broad trapezium-like peak between 680 and 1050 K.  $\text{H}_2$  evolved as a weak peak with a maximum that coincided with the maximum of the CO peak and the minimum of the  $\text{H}_2\text{O}$  yield. The  $\text{H}_2$  formation

increased again at  $\sim 1020$  K when the  $\text{H}_2\text{O}$  formation decreased. Such product distribution indicates that both total (1) and partial (2) oxidation of propylene occur.



In contrast, in oxygen excess ( $R = 10$ ), a sharp strong peak of  $\text{CO}_2$  with a maximum at  $\sim 470$  K was observed. The peak was asymmetric with a high temperature shoulder. In addition, a low-intensity peak at  $\sim 820$  K was observed. The formation of  $\text{CO}$  was observed only above  $\sim 600$  K and slightly increased with temperature. No  $\text{H}_2$  yield was detected at temperatures below  $\sim 1150$  K. Similar TPRS profiles were observed at  $R$  equal to 100 as well (not shown here). It means that during the heating of the Pd(551) single crystal in excess of oxygen, the total oxidation of propylene to  $\text{CO}_2$  and water dominates.



**Fig. 1.**  $\text{H}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{CO}$ , and  $\text{CO}_2$  TPRS profiles obtained during heating (upper panels) and cooling (lower panels) of Pd(551) in reaction mixtures with different molar oxygen/propylene ratios  $R$  equal to 1, 3, and 10, respectively. The partial pressure of propylene was  $1 \times 10^{-7}$  mbar. The curves were shifted vertically for better visualization.

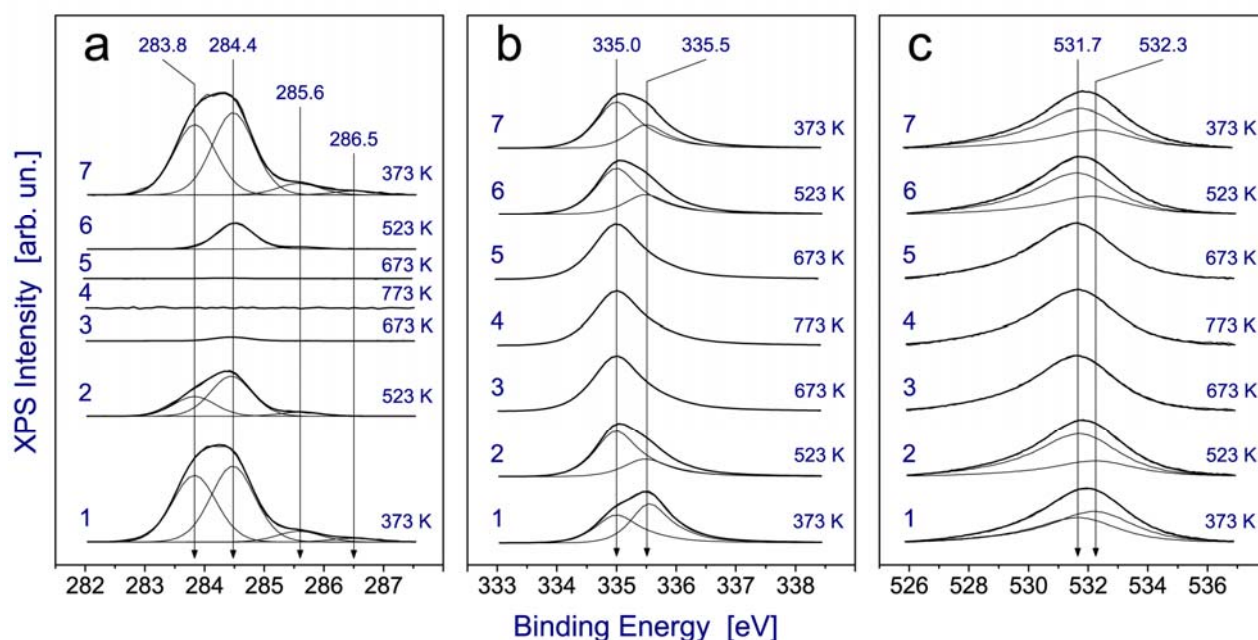
An intermediate picture was observed at  $R = 3$ , both  $\text{CO}$  and  $\text{CO}_2$  were formed in appreciable amounts during heating.  $\text{CO}_2$  production exhibited an asymmetric peak with a maximum at  $\sim 540$  K, a small shoulder at  $\sim 490$  K and a lengthy shoulder at higher temperatures. A low-intensity peak was visible at  $\sim 800$  K as well.  $\text{CO}$  formation showed a sharp intense peak with a maximum at  $\sim 520$  K. The full width at half maximum of the peak was only 35 degrees, and, hence, it can be called a “surface explosion” [24-26]. Surface explosions have been studied in detail for the

NO+CO reaction over Pt(100), where the platinum surface undergoes a change between a state with a low catalytic activity (where a high adsorbate coverage inhibits the dissociation of adsorbed NO) and a state with a high catalytic activity (where a low surface coverage allows NO dissociation) [25]. Most likely that in our case, the surface at low temperatures was blocked by carbon atoms and no reaction products were formed; whereas at higher temperatures, carbon atoms started to react with oxygen atoms to produce free sites for further oxygen adsorption and reaction.

In all the TPRS profiles obtained during cooling, the CO<sub>2</sub> formation appeared as a broad peak, which looked like an unresolved doublet. Under oxygen-lean conditions (R = 1), the first peak of the doublet appeared at ~510 K and its maximum shifted to lower temperatures (to ~490 and ~480 K) with an increase in the oxygen content. The second peak of the doublet was near 750 K and its maximum shifted to higher temperatures (to ~810 and ~820 K) with an increase in the oxygen content. CO formation was observed above 470 K and the CO yield increased with temperature. Water was produced at temperatures above 310-350 K. A minor yield of H<sub>2</sub> was only detected at temperatures above 1050 and 1090 K for R equal to 1 and 3, respectively, when the H<sub>2</sub>O yield decreased.

Earlier, a temperature hysteresis has been observed for different oxidation reactions both over supported and unsupported palladium catalysts. A classic example is the temperature hysteresis in activity for the total oxidation of methane over Pd-based catalysts [7,11-14,17]. Another well-known example is the temperature hysteresis for the oxidation of CO over Pd-based catalysts [27]. In both cases, high and low activity states of the catalysts were associated with reduced and oxidized states of palladium [12,27]. A more complex temperature hysteresis was observed in the oxidation of ethene over Pd(111) [15,16]. Recently, Gabasch et al. [16], using molecular beam TPR techniques, have found that under oxygen-lean conditions, in a pressure range of 10<sup>-7</sup>-10<sup>-6</sup> mbar, the main reaction pathway was the partial oxidation of ethene. They have shown that the dominant reaction product was CO, and that CO<sub>2</sub> formation did not exceed 10 % in a temperature range of 370-970 K at a molar ratio O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> of 3. In contrast to our results, increasing the oxygen content in the reaction mixture resulted in deactivation of the palladium surface and the total reaction rate was almost zero below 750 K at a molar ratio O<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> of 10. It indicates that the rate of the oxidation of propylene over Pd(551) is noticeably higher than the rate of the oxidation of ethene over Pd(111) because in our experiments the yield of CO<sub>2</sub> has been detected even at R equal to 100 (not shown). Most probably, this difference is controlled by the surface structure, and the stepped surface of Pd(551) with many regular defects is more active in the oxidation of hydrocarbons than the flat surface of Pd(111) [23]. At the same time, the different adsorption properties of propylene and ethene can also affect on the reaction rate.

Gabasch et al. [16] also observed that under oxygen-lean conditions, a temperature hysteresis occurred during the oxidation of ethene: the CO yield during heating and cooling did not coincide. On the heating branch, CO evolved as a well-defined peak with a maximum at  $\sim 520$  K followed by a minimum at  $\sim 670$  K, then the CO formation rate increased again. On the cooling branch, the CO peak did not appear and the CO formation rate decreased with decreasing temperature at the molar ratio  $O_2/C_2H_4$  of 5 [16]. The authors suggested that the palladium surface is deactivated by adsorbed oxygen species ( $O_{ads}$ ) and that an oxygen-free metal surface, where ethene can dissociate, is necessary for a high activity [16]. Since carbon species produced via the hydrocarbon decomposition can dissolve in the Pd bulk and then segregate at the Pd surface [15,21,28], the temperature hysteresis may be due to a temperature- and time-dependent interplay of segregation and re-segregation of carbon and oxygen adsorbed species [16].



**Fig. 2.**  $Cl_{1s}$  (a),  $Pd3d_{5/2}$  (b), and  $O_{1s}/Pd3p_{3/2}$  (c) core-level spectra obtained during stepwise heating (spectra 1, 2, 3, and 4) and subsequent cooling (spectra 5, 6, and 7) of Pd(551) in the reaction mixture under oxygen-lean conditions ( $R = 1$ ).

This mechanism might explain the temperature hysteresis observed in other oxidative reactions over palladium. However, the applicability of this mechanism for the oxidation of propylene is not straightforward, because the product distributions observed for the oxidation of propylene and ethene are different. To elucidate the mechanism for the temperature hysteresis in the oxidation of propylene, *in situ* XPS has been applied. Taking into account the TPRS data, which pointed to the negligible activity of palladium at low temperatures, the XPS study was performed in a temperature range between 373 and 773 K. Fig. 2 presents the  $Cl_{1s}$ ,  $Pd3d_{5/2}$ , and  $O_{1s}/Pd3p_{3/2}$  core-level spectra of the palladium surface obtained during stepwise heating at 373, 523, 673, and 773 K



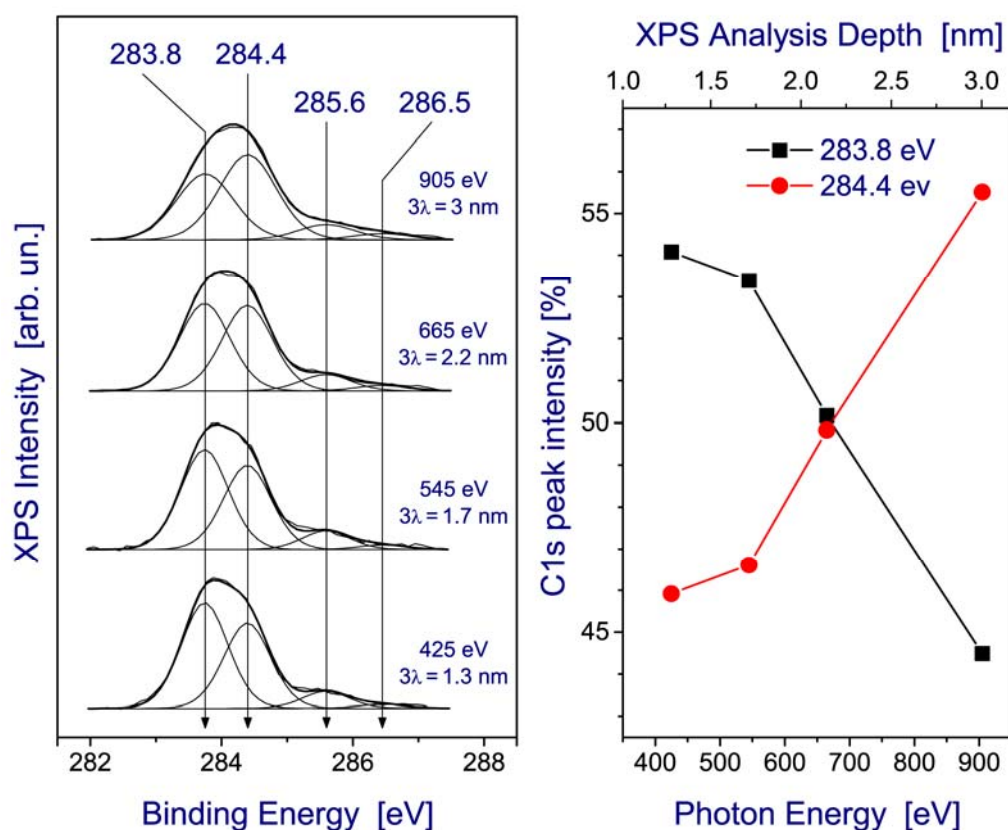
and during subsequent cooling in the same manner in the reaction mixture under oxygen-lean conditions ( $R = 1$ ).

The  $C1s$  spectrum obtained at 373 K consists of two intense peaks at 283.8 and 284.4 eV and two weak peaks at 285.6 and 286.5 eV. The first two peaks correspond to the carbon species adsorbed on the surface and dissolved in the Pd bulk [15,21,28]. Indeed, this temperature is sufficient for the dissociative adsorption of propylene, resulting in the formation of carbon species on the surface. Earlier, it was shown that on Rh(111) propylene adsorbs intact at 80 K while above 270 K propylidyne ( $CCH_2CH_3$ ) is formed [29]. At room temperature, propylidyne decomposes to ethylidyne ( $CCH_3$ ), which is stable up to 400 K. Above this temperature decomposition to  $CH_x$  fragments was observed. According to previous SFG/XPS studies [28], the  $CH_x$  species completely dehydrogenate on palladium even at room temperature. Therefore, we assume that at 373 K propylene decomposes on Pd(551) to produce atomic carbon species, which can dissolve in the near-surface region of palladium to form a  $PdC_x$  phase. This effect was discovered by Ziemecki et al. [30]. They found that the interstitial  $PdC_x$  phase can be formed upon interaction of palladium with various carbon-containing molecules. According to DFT calculations [31], the migration of carbon atoms from the surface hollow sites into the octahedral subsurface sites of Pd is almost an isoenergetic process. Approximately 13 % of the octahedral subsurface sites of Pd can be occupied by carbon. This  $PdC_x$  phase is metastable and decomposes above 900 K in an inert atmosphere and at 450 K in  $O_2$  [30].

In our case, the formation of the  $PdC_x$  phase was confirmed by the  $Pd3d_{5/2}$  spectrum, which consists of a peak at 335.5 eV in addition to a peak at 335.0 eV (Fig. 2). The latter corresponds to Pd in the metallic state, while the former can be assigned to the  $PdC_x$  phase. Previously, the appearance of the  $Pd3d_{5/2}$  peak at 335.3 eV originating from the  $PdC_x$  phase was observed during carbon incorporation into the near-surface region of Pd during the oxidation of ethene [15]. In order to assign the  $C1s$  peaks at 283.8 and 284.4 eV to the adsorbed carbon species and the dissolved carbon species, depth profiling of the  $C1s$  spectra was performed by varying the incident photon energy. Because the mean free path of electrons ( $\lambda$ ) in a solid depends on their kinetic energy (KE), the escape depth of photoelectrons varies with the incident photon energy ( $h\nu$ ) according to the law of energy conservation,  $KE = h\nu - BE$ . The  $C1s$  spectra obtained *in situ* during the oxidation of propylene at 373 K using four different incident photon energies of 425, 545, 665, and 905 eV are presented in Fig. 3. These energies correspond to inelastic mean free path lengths of 4.4, 5.8, 7.2, and 10 Å. These values were calculated using the QUASES-IMFP-TPP2M software [32,33] under assumption that palladium remains the predominant constituent in the near-surface region. Since the core-level spectra were collected at normal emission of photoelectrons, and the electron intensity exponentially decays with the sampling volume, according to the well-known Beer-Lambert

formalism, the XPS analysis depth can be estimated as  $3\lambda$ , and therefore these energies correspond to the analysis depths approximately equal to 13, 17, 22, and 30 Å, respectively.

One can see that the *C1s* spectra consist of two high-intensity peaks at 283.8 and 284.4 eV and two low-intensity peaks at 285.6 and 286.5 eV (Fig. 3). As to mention above, the first two peaks correspond to carbon species adsorbed on the surface and/or dissolved in the Pd bulk, while the last low-intensity peaks correspond to CO adsorbed species and carbon atoms in surface oxygenates, respectively [15,19-21,28]. The relative intensity of the *C1s* peak at 283.8 eV increases with decreasing the incident photon energy from 905 to 425 eV, whereas the intensity of the *C1s* peak at 284.4 eV changes in the reverse manner. Correspondingly, the *C1s* peak at 283.8 eV can be assigned to carbon species adsorbed on the surface ( $C_{ads}$ ), while the *C1s* peak at 284.4 eV can be attributed to carbon species dissolved in the bulk of palladium.



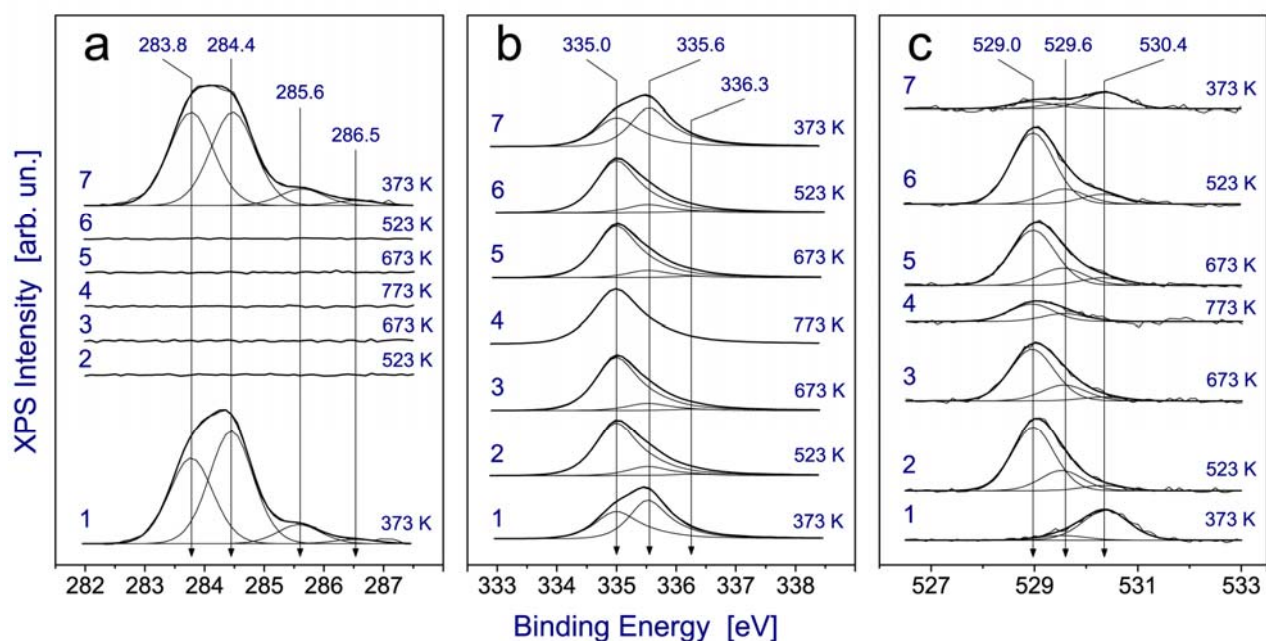
**Fig. 3.** *C1s* core-level spectra obtained *in situ* during the oxidation of propylene over Pd(551) at 373 K using different photon energies: 425, 545, 665, and 905 eV, respectively (left panel). Relative intensities of the *C1s* peaks at 283.8 and 284.4 eV depending on the photon energy (right panel). The molar oxygen/propylene ratio is equal to 10.

Hence, the intense peaks at 283.8 and 284.4 eV observed at 373 K under oxygen-lean conditions ( $R = 1$ ) were attributed to carbon species adsorbed on the surface and to dissolved carbon species, respectively; the other peaks at 285.6 and 286.5 eV can be attributed to different

oxygen-containing species (Fig. 2). According to the literature data [15,19-21,28], the peak at 285.6 eV corresponds to adsorbed CO species, while the peak at 286.5 eV, most likely, corresponds to carbon atoms in the ketone or carboxylate species. The latter peak disappeared at 523 K. The CO peak decreased at 523 K and disappeared at higher temperatures. The peaks at 283.8 and 284.4 eV also decreased during heating: at 523 K, their intensities dropped by a factor of  $\sim 3$ . At 673 K, these peaks were negligible and, at 773 K, there were no peaks in the *C1s* spectrum. Note that during the acquisition of the core-level spectra at 523 K, the *C1s* peaks slowly decreased in intensity, indicating that this temperature is critical for these conditions. At other temperatures the *C1s* peaks were stable.

During cooling, only a single peak at 284.4 eV appeared in the *C1s* spectrum at 523 K (Fig. 2). Since the *Pd3d<sub>5/2</sub>* peaks at 335.0 and 335.5 eV were also observed, this *C1s* peak can be attributed to dissolved carbon atoms. At 373 K, all the *C1s* peaks restored their intensities. This is an important finding that conflicts with results of previous *in situ* XPS/TRPS studies concerning the oxidation of ethene over Pd(111) [15]. In Ref. 15 it was reported that the  $\text{PdC}_x$  phase has a high selectivity toward CO, whereas our data (Fig. 2) suggest that the selectivity toward  $\text{CO}_2$  at 523 K changes appreciably during cooling and heating although dissolved carbon species were detected by XPS in both cases. Therefore, we supposed that the pronounced shift of the selectivity toward  $\text{CO}_2$  during the oxidation of propylene is due to an increasing concentration of oxygen on the palladium surface while the formation of the  $\text{PdC}_x$  phase does not affect the selectivity. This idea is supported indirectly by the fact that during heating, a high surface concentration of  $\text{C}_{\text{ads}}$  at 523 K (Fig. 2) is accompanied with a low yield of  $\text{CO}_2$  (Fig. 1).

Unfortunately, due to the overlap of the *O1s* and *Pd3p<sub>3/2</sub>* spectra and low concentration of oxygen, we could not analyze the *O1s* spectra under oxygen-lean conditions. Only two peaks at 531.7 and 532.3 eV were observed in the *O1s/Pd3p<sub>3/2</sub>* core-level spectra (Fig. 2), which correspond mainly to the *Pd3p<sub>3/2</sub>* peaks of the palladium atoms in the metallic state and in the  $\text{PdC}_x$  phase, respectively. Indeed, the relative intensity and shift of these peaks corresponded to the structure of the *Pd3d<sub>5/2</sub>* spectra. At the same time, the *O1s* peaks were distinguished evidently in the spectra obtained *in situ* under the oxygen-rich conditions (Fig. 4). The three peaks observed at 529.0, 529.6, and 530.4 eV in the spectra could be attributed to chemisorbed oxygen species, a surface oxide, bulk PdO, dissolved oxygen species or oxygen in different functional groups. A surface oxide similar to a  $\text{Pd}_5\text{O}_4$  surface oxide [17], which can be formed on the Pd(111) surface, may be characterized by similar values of the *O1s* binding energy. It is well known that the identification of different oxygen species based on the *O1s* spectra is a very difficult task [34]. Nevertheless, the joint analysis of the *O1s*, *C1s*, and *Pd3d* spectra allowed us to draw some conclusions about the origin of the oxygen species observed during the oxidation of propylene over palladium.



**Fig. 4.**  $C1s$  (a),  $Pd3d_{5/2}$  (b), and  $O1s$  (c) core-level spectra obtained during stepwise heating (spectra 1, 2, 3, and 4) and subsequent cooling (spectra 5, 6, and 7) of Pd(551) in the reaction mixture ( $R = 10$ ). The  $O1s$  spectra were obtained after subtraction of the corresponding  $Pd3p_{3/2}$  core-level spectra as described elsewhere [38].

Since the  $C1s$  spectrum at 373 K (Fig. 4a), in addition to the strong peaks at 283.8 and 284.4 eV, exhibits the peaks at 285.6 and 286.5 eV corresponding to adsorbed CO and surface oxygenates, the strong  $O1s$  peak at 530.4 eV (Fig. 4c) can be attributed to oxygen atoms bonded to carbon atoms. This is confirmed by the fact that at 523 K, this  $O1s$  peak decreased in intensity and all the  $C1s$  peaks simultaneously disappeared. In support to this statement, methoxy groups adsorbed on copper, for instance, are characterized by the  $O1s$  peak at 530.9 eV [35]. Two other peaks at 529.0 and 529.6 eV observed at 373 K can be attributed to different  $C_xO_y$  adsorbed species as well. Similar values of the  $O1s$  binding energy are also observed for adsorbed and dissolved atomic oxygen species and for  $Pd_5O_4$  surface oxide [36-38]. However, the presence of large amounts of dissolved oxygen species is unlikely because the characteristic features of the  $PdC_x$  phase are clearly observed in the  $Pd3d_{5/2}$  spectra (Fig. 4b). The oxygen and carbon dissolved species compete with each other because only a small part of the octahedral sites of palladium can be occupied. Moreover, the dissolution of oxygen in palladium is limited by kinetic factors because the rate of this process is negligible at moderated temperature [39].

We do not exclude a moderate amount of a 2D palladium oxide, like  $Pd_5O_4$ , which can exist on the surface in the form of small islands. It should be noted that to the best of our knowledge no experimental data about a formation of the 2D oxide on Pd(551) are published elsewhere. However, the formation of surface oxides such as  $Pd_5O_4$  over Pd(111) is not a unique phenomenon. For

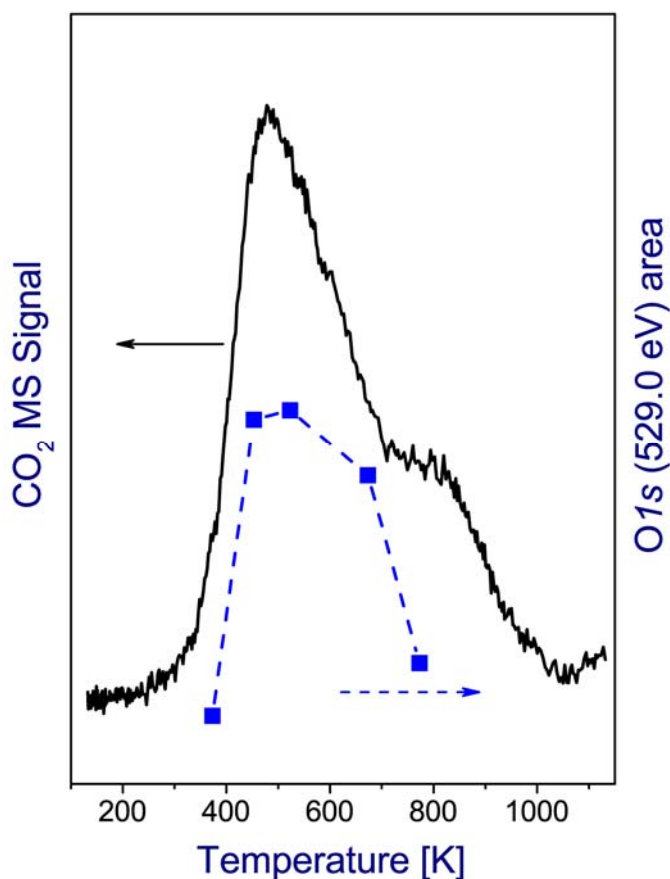
example, surface oxides that are characterized with a  $c(6\times 2)$  LEED pattern and an oxygen coverage of close to 1 ML were observed on Cu(110) and Ag(110) [40-42]. The  $c(6\times 2)$ O structure consists of two different oxygen species on Ag(110) that are characterized by two vibrational loss peaks at 298 and 339  $\text{cm}^{-1}$  [42]. Because the Pd(551) surface consists of three-atomic terraces of the (110) plane divided by (111) steps, we believe that a similar surface oxide can be formed in our case as well. For detailed study of the surface oxide formation on Pd(551), additional experiments are necessary.

It is very important to note that no peaks in the *Cl*s spectra (Fig. 4a) are observed at higher temperatures and, correspondingly, the peaks at 529.0, 529.6, and 530.4 eV in the *O*1s spectra point to the presence of different Pd-O species. This finding confirms that at low temperatures, the palladium surface is inactive in the oxidation of hydrocarbons because of carbon deposits that block the surface and prevent the adsorption of oxygen [21]. Heating accelerates the mobility of carbon atoms on the surface and in the subsurface layers of palladium; this creates free sites for oxygen adsorption and, as a result, the reaction starts at temperatures near 470 K. The intense peak at 529.0 eV in the *O*1s spectra obtained at 523 and 673 K (Fig. 4c) can be attributed to oxygen atoms adsorbed on the palladium surface [38]. Since the Pd3*d*<sub>5/2</sub> spectra exhibit weak peaks at 335.6 and 336.3 eV, a small amount of the 2D palladium oxide also exists on the surface. Correspondently, the *O*1s peaks at 529.0 and 529.6 eV can be attributed to oxygen in the surface oxide. According to literature data [36,37], oxygen atoms with different local environment in the Pd<sub>5</sub>O<sub>4</sub> structure on Pd(111) are characterized by the *O*1s binding energies of 528.9-529.0, 529.5-529.6, and 530.4 eV. The dissolved oxygen usually forms at higher temperatures [36]. No bulk PdO was formed under all conditions used since we did not observe its characteristic peak at 336.8 eV in the Pd3*d*<sub>5/2</sub> spectra [43].

Thus, the peak at 529.0 eV observed in the *O*1s spectra can be attributed mainly to oxygen atoms adsorbed on the palladium surface. A comparison of the CO<sub>2</sub> yield during cooling Pd(551) in the reaction mixture with the relative concentration of the adsorbed oxygen species, which was estimated from the area of the *O*1s peak at 529.0 eV, is presented in Fig. 5. Apparently, these data correlate well. It should be noted, that no transition effects during the acquisition of the *O*1s spectra were observed.

Hence, we can conclude, that the active state of palladium in the total oxidation of propylene can be attributed to palladium in the metallic state with a high concentration of chemisorbed oxygen and a moderate amount of the 2D oxide on the surface. The low active state is associated with palladium in the metallic state covered by carbon deposits. The temperature hysteresis in activity and selectivity is caused by a concurrent accumulation of carbon and oxygen atoms on the palladium surface. The molar propylene/oxygen ratio in the reaction mixture has a large effect on the rates of these processes. As a result, the first CO<sub>2</sub> peak shifts from 510 to 480 K on the cooling

branches with increasing oxygen content (Fig. 1). The shift of the second CO<sub>2</sub> peak in the opposite direction from 750 to 820 K may be related to the formation of the 2D palladium oxide: increasing the partial pressure of O<sub>2</sub> shifts the balance between the rates of the formation and decomposition of the surface palladium oxide to higher temperatures. The shift of the selectivity toward CO<sub>2</sub> is the result of an increasing concentration of oxygen on the palladium surface.



**Fig. 5.** CO<sub>2</sub> yield versus temperature during cooling the Pd(551) single crystal in the reaction mixture (R = 10) and the area of the O1s peak at 529.0 eV measured at the same conditions.

#### 4. Summary and conclusions

The presented data clearly indicate that the product distribution and activity depend in a different way on the temperature during heating and cooling the Pd(551) single crystal in oxygen/propylene mixtures. By comparing the TPRS and XPS data, we can suggest that this unusual kinetic behavior, referred to as temperature hysteresis, is induced by the concurrent accumulation of carbon and oxygen atoms on the palladium surface. At low temperatures, a high concentration of carbonaceous deposits results in a low catalytic activity because of blocking of the palladium surface. Increasing temperature led to full dehydrogenation of the carbonaceous species to carbon and dissolution of carbon atoms into subsurface palladium layers. As a result, the PdC<sub>x</sub> phase was formed at 373 K even under oxygen-rich conditions. This process had no influence on

the selectivity in the oxidation of propylene at least under UHV conditions. It was found that the observed shift of selectivity toward CO<sub>2</sub> is the result of an increase in the oxygen concentration on the palladium surface. The state with a low activity in the oxidation of propylene is associated with palladium in the metallic state covered by carbonaceous deposits. The high-active state of palladium is associated with metallic palladium with a high concentration of chemisorbed oxygen and a moderate amount of a 2D palladium oxide. The concentration of bulk PdO was negligible in the entire temperature range. Certainly, some additional experiments at higher pressures need to be performed in order to elucidate further the mechanism for the oxidation of hydrocarbons over palladium. In particular, it will allow a comparison of the catalytic properties of a surface palladium oxide with those of bulk PdO, which can be formed at elevated pressures. We plan to carry out *in situ* XPS studies of the oxidation of propylene over palladium in the millibar pressures in the near future.

### **Acknowledgments**

This work was partially supported by the Russian Foundation for Basic Research (Research project No. 12-03-00766-a) and the Ministry of Education and Science of the Russian Federation. The authors are also grateful to M. Hävecker, D. Teschner, and R. Blume as well as the staff of BESSY for their support during the beamtime. The authors would like to thank C.J. Weststrate and J.W. Bakker for helpful discussions and technical support.

### **References**

- [1] K.C. Taylor, *Catal. Rev. – Sci. Eng.* 35 (1993) 457.
- [2] M. Shelef, R.W. McCabe, *Catal. Today* 62 (2000) 35.
- [3] M.V. Twigg, *Appl. Catal. B* 70 (2007) 2.
- [4] D. Ciuparu, M.R. Lyubovsky, E. Altman, L.D. Pfefferle, A. Datye, *Catal. Rev. – Sci. Eng.* 44 (2002) 593.
- [5] E.I. Altman, *Surf. Sci.* 547 (2003) 108.
- [6] K. Eguchi, H. Arai, *Appl. Catal. A* 222 (2001) 359.
- [7] Y. Deng, T.G. Nevell, *J. Mol. Catal. A* 142 (1999) 51.
- [8] G.W. Graham, D. König, B.D. Poindexter, J.T. Remillard, W.H. Weber, *Top. Catal.* 8 (1999) 35.
- [9] X. Zhang, C.S.-M. Lee, D.M.P. Mingos, D.O. Hayward, *Appl. Catal. A* 240 (2003) 183.
- [10] V.Yu. Bychkov, Yu.P. Tyulenin, M.M. Slinko, V.N. Korchak, *Catal. Lett.* 141 (2011) 602.
- [11] P. Salomonsson, S. Johansson, B. Kasemo, *Catal. Lett.* 33 (1995) 1.
- [12] P. Gelin, M. Primet, *Appl. Catal. B* 39 (2002) 1.
- [13] J.-D. Grunwaldt, N. van Vegten, A. Baiker, *Chem. Commun.* (2007) 4635.

- [14] G. Centi, *J. Mol. Catal. A* 173 (2001) 287.
- [15] H. Gabasch, E. Kleimenov, D. Teschner, S. Zafeiratos, M. Hävecker, A. Knop-Gericke, R. Schlögl, D. Zemlyanov, B. Aszalos-Kiss, K. Hayek, B. Klötzer, *J. Catal.* 242 (2006) 340.
- [16] H. Gabasch, A. Knop-Gericke, R. Schlögl, W. Unterberger, K. Hayek, B. Klötzer, *Catal. Lett.* 119 (2007) 191.
- [17] H. Gabasch, K. Hayek, B. Klötzer, W. Unterberger, E. Kleimenov, D. Teschner, S. Zafeiratos, M. Hävecker, A. Knop-Gericke, R. Schlögl, B. Aszalos-Kiss, D. Zemlyanov, *J. Phys. Chem. C* 111 (2007) 7957.
- [18] V.V. Gorodetskii, A.V. Matveev, E.A. Podgornov, F. Zaera, *Top. Catal.* 32 (2005) 17.
- [19] V.I. Bukhtiyarov, V.V. Kaichev, I.P. Prosvirin, *Top. Catal.* 32 (2005) 3.
- [20] A. Knop-Gericke, E. Kleimenov, M. Hävecker, R. Blume, D. Teschner, S. Zafeiratos, R. Schlögl, V.I. Bukhtiyarov, V.V. Kaichev, I.P. Prosvirin, A.I. Nizovskii, H. Bluhm, A. Barinov, P. Dudin, M. Kiskinova, *Adv. Catal.* 52 (2009) 213.
- [21] V.V. Kaichev, A.V. Miller, I.P. Prosvirin, V.I. Bukhtiyarov, *Surf. Sci.* 606 (2012) 420.
- [22] A.V. Miller, V.V. Kaichev, I.P. Prosvirin, V.I. Bukhtiyarov, *J. Phys. Chem. C* 117 (2013) 8189.
- [23] D. Ferrer, D.A. Blom, L.F. Allard, S. Mejia, E. Perez-Tijerina, M. Jose-Yacaman, *J. Mater. Chem.* 18 (2008) 2442.
- [24] Th. Fink, J.P. Dath, R. Imbihl, G. Ertl, *J. Chem. Phys.* 95 (1991) 2109.
- [25] S.J. Alas, L. Vicente, *J. Chem. Phys.* 128 (2008) 134705.
- [26] A.V. Matveev, A.A. Sametova, V.V. Gorodetskii, *Kinet. Catal.* 45 (2004) 598.
- [27] I. Yuranov, L. Kiwi-Minsker, B. Barelko, A. Renken, *Study Surf. Sci. Catal.* 122 (1999) 191.
- [28] M. Morkel, V.V. Kaichev, G. Rupprechter, H.-J. Freund, I.P. Prosvirin, V.I. Bukhtiyarov, *J. Phys. Chem. B* 108 (2004) 12955.
- [29] B.E. Bent, C.M. Mate, J.E. Crowell, B.E. Koel, G.A. Somorjai, *J. Phys. Chem.* 91 (1987) 1493.
- [30] S.B. Ziemecki, G.A. Jones, D.G. Swartzfager, R.L. Harlow, *J. Am. Chem. Soc.* 107 (1985) 4547.
- [31] I.V. Yudanov, K.M. Neyman, N. Rösch, *Phys. Chem. Chem. Phys.* 6 (2004) 116.
- [32] <http://www.quases.com/>
- [33] S. Tanuma, C. J. Powell, D. R. Penn, *Surf. Interf. Anal.* 21 (1994) 165.
- [34] V.I. Bukhtiyarov, M. Hävecker, V.V. Kaichev, A. Knop-Gericke, R.W. Mayer, R. Schlögl, *Phys. Rev. B* 67 (2003) 235422.
- [35] A.F. Carley, A.W. Owens, M.K. Rajumon, M.W. Roberts, S.D. Jackson, *Catal. Lett.* 37 (1996) 79.



- [36] D. Zemlyanov, B. Klötzer, H. Gabasch, A. Smeltz, F.H. Ribeiro, S. Zafeiratos, D. Teschner, P. Schnörch, E. Vass, M. Hävecker, A. Knop-Gericke, R. Schlögl, *Top. Catal.* 56 (2013) 885.
- [37] D. Zemlyanov, B. Aszalos-Kiss, E. Kleimenov, D. Teschner, S. Zafeiratos, M. Hävecker, A. Knop-Gericke, R. Schlögl, H. Gabasch, W. Unterberger, K. Hayek, B. Klötzer, *Surf. Sci.* 600 (2006) 983.
- [38] F.P. Leisenberger, G. Koller, M. Sock, S. Surnev, M.G. Ramsey, F.P. Netzer, B. Klötzer, K. Hayek, *Surf. Sci.* 445 (2000) 380.
- [39] J. Han, D.Y. Zemlyanov, F.H. Ribeiro, *Surf. Sci.* 600 (2006) 2752.
- [40] D. Coulman, J. Wintterlin, J.V. Barth, G. Ertl, *Surf. Sci.* 240 (1990) 151.
- [41] G. Dorenbos, D.O. Boerma, *Surf. Sci.* 287-288 (1993) 443.
- [42] S.R. Bare, K. Griffiths, W.N. Lennard, H.T. Tang, 342 (1995) 185.
- [43] R.S. Monteiro, D. Zemlyanov, J.M. Storey, F.H. Ribeiro, *J. Catal.* 201 (2001) 37.