In situ XPS study of self-sustained oscillations in catalytic oxidation of propane over nickel

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A B S T R A C T

Self-sustained oscillations in the propane oxidation over a nickel foil were studied in situ with the use of ambient-pressure X-ray photoelectron spectroscopy (XPS) coupled with on-line mass-spectrometry and gas chromatography (GC). Regular oscillations of a relaxation type were observed at 0.5 mbar in the temperature range of 600–750ºC in oxygen-deficient conditions. CO, CO_2, H_2, H_2O, and propylene were detected as products. CO selectivity in active half-periods achieved 98% decreasing to 40–60% in inactive half-periods. It has been found that the chemical state of the catalyst drastically changes together with the oscillations of the catalytic activity. According to the Ni$2p$ and O$1s$ core-level spectra measured in situ, the active catalyst surface is represented by metallic nickel, whereas it is covered with a layer of NiO with a thickness of at least 3 nm during the inactive half-periods. It means that the oscillations in the propane oxidation over nickel are originated from the reversible bulk oxidation of Ni to NiO. We suggest that the propane oxidation over the metallic Ni surface occurs via the Langmuir–Hinshelwood mechanism, whereas the Mars–van Krevelen mechanism prevails when the reaction proceeds over NiO. The switching between the metallic surface and the oxide shows a significant change in the catalytic activity. According to GC measurements the activity of metallic nickel is approximately 40-fold higher than that of NiO.

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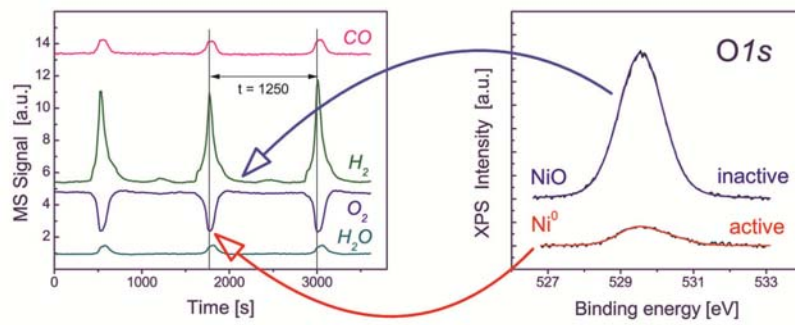
1. Introduction

It is well-known that under certain conditions many heterogeneous catalytic reactions exhibit rate oscillations [1–5]. To date the self- sustained oscillations have been discovered in approximately 40 catalytic reactions in a wide range of pressures from ultrahigh vacuum (UHV) up to atmospheric pressure. It has been shown that this unusual phenomenon can appear as sinusoidal or harmonic oscillations, as relaxation-type oscillations, as well as chaos. It should be noted that the relaxation oscillations, in contrast to the harmonic ones, are characterized by two quite different time scales and can be described as fast evolution (jump up and jump down) between "low-active" and "high-active" states. The oscillations can be observed both in isothermal and in non-isothermal conditions. In some cases the kinetic oscillations are accompanied by a spatiotemporal self-organization in surface reactions that has been observed in detail by modern microscopic techniques [6,7].

Many efforts have been spent in recent years to observe and to analyze the self-sustained oscillations in different catalytic reactions. However, overwhelming majority of the investigations was devoted to study the oscillation mechanism in the simplest catalytic systems such as the CO oxidation over Pt and Pd single-crystal surfaces in UHV. The experimental results of these studies have stimulated appearance of numerous theoretical models which not only explained the origin of the kinetic instabilities, but also tried to predict the oscillatory behavior under certain conditions [3]. However, these models cannot be directly applied for more complicated reactions, such, for instance, as oxidation of light alkanes over VIII group metals.

The self-sustained oscillations of the methane oxidation rate have been observed over a great variety of catalysts including Ni wires, foils, and foams, Ni/Cr alloys, Co foils, Pd films and foils, as well as Ni, Pd, Rh, and Ru supported particles [8–24]. Recently, the rate oscillations of the ethane oxidation over Ni, Co, and Pd foils have been also reported [25,26]. Our previous works have shown that the regular oscillations with a period of several minutes can be also realized for the partial oxidation of propane to synthesis gas over nickel at pres- sures of approximately 1 mbar [27,28]. For all aforementioned hydro- carbons the relaxation oscillations of concentrations of both reactants and products as well as the oscillations of the catalyst temperature have been observed. Other general peculiarity for the reactions was the fact that the stable repeatable oscillations in the oxidation of light alkanes appeared after an induction period which was characterized by a low catalytic activity and varied from several minutes to a few

hours. During the induction period a rough, highly-porous structure of the subsurface catalyst layers was produced on the catalyst surface [11,27]. Therefore, the rate oscillations are likely to be associated with slow reversible transformation of the catalyst surface. Similarity in oscillation patterns in all mentioned catalytic systems allowed us to suggest their common origin.

Numerous mechanisms describing the rate oscillations for different heterogeneous catalytic reactions were proposed over the last 30 years [1–5]. However, only three hypotheses can explain the rate oscillations of the oxidation of light alkanes over transition metal catalysts, namely a reconstruction model [29], a carbon model [30], and an oxide model [31]. The first model was drawn from the results of the ultrahigh-vacuum study of the CO oxidation over Pt single-crystal surfaces. The rates of CO and oxygen adsorption vary due to the surface reconstruction and depend on the adsorption layer composition. Another typical example of the reconstruction case is the partial oxidation of methanol to formaldehyde over silver catalysts. In this reaction surface reconstruction strongly affects the oxygen adsorption characteristics, which in turn influence the catalyst performance [32]. Strong reaction-induced changes of the catalyst morphology were also observed under ambient pressure in other catalytic systems [33–35]. The other two models link the rate oscillations to a periodic deactivation of the catalyst surface either due to the accumulation of carbonaceous deposits or due to the formation of a surface oxide layer.

This study was performed to discriminate between these three models and to obtain information about the chemical state of the catalyst surface under the oxidation of light alkanes in the self-oscillation regime. To achieve this goal, ambient-pressure X-ray photoelectron spectroscopy, which is one of the most useful tools to investigate the surface composition and the nature of adsorbed species [36,37], was chosen. Its combination with mass-spectrometry (MS), which can monitor the gas-phase composition, becomes a particularly effective in situ technique, making it possible to correlate the surface composition with the catalyst performance.

Since the catalytic oxidation of propane over nickel exhibits oscillatory behavior in the millibar pressure range, that is the upper limit for in situ measurements with XPS, namely this reaction was chosen for the case investigation. In the current study we used the combined ambient-pressure XPS–MS approach to detect the chemical state of the surface of the nickel foil during the active and inactive half-periods of oscillations in the propane oxidation. In some experiments the product composition was also analyzed by on-line gas-chromatography.

2. Experimental details

The experiments were performed at the ISISS beamline at the Berlin electron storage ring for synchrotron radiation (BESSY II). The experimental setup was described in detail elsewhere [37]. A key feature of this setup, which makes it possible to acquire photoelectron spectra under millibar pressure, is the differential pumping between a high-pressure cell and an electron energy analyzer (PHOIBOS-150, SPECS). The high-brilliance synchrotron radiation along with a short travel path of the photoelectrons through the high-pressure zone allows us to obtain the high-quality photoelectron spectra at pressures up to 2 mbar. All spectra were normalized to the incident photon flux and to the ring current. The photoelectron take-off angle (measured from the sample surface) was 90°. The binding energy was referenced to the Fermi edge in the valence-band spectra of a metallic nickel for each experiment. The Ni$2p_{3/2}$, O$1s$, and C$1s$ spectra were usually obtained using the photon energies of 1050, 730, and 485 eV, respectively, that provides the same kinetic energy (approximately 200 eV) for each region. This is important to assure the same information depth for all elements. In depth profiling experiments, the kinetic energy of the Ni$2p$ photoelectrons varied from 200 eV to approximately 500 eV, when the photon energy was 1350 eV. The spectra were curve-fitted after a Shirley-type background subtraction. The line-shape was assumed to be a mixture of Gaussian and Lorentzian functions. To fit the Ni$2p_{3/2}$ spectrum from the active surface, an analytical Doniach-Sanjic function convolved with Gaussian was used [38].

The propane and oxygen flows were regulated separately with calibrated mass-flow controllers. In all experiments, the oxygen flow was 0.65 sccm, while the propane flow was varied in the range of 1.9-9.3 sccm depending on the required propane/oxygen ratio. The total pressure of reaction mixtures in the high-pressure cell was kept at a constant level of 0.5 mbar. The gas-phase composition was monitored continuously with an on-line quadrupole mass-spectrometer (Prizma QMS-200, Pfeiffer) connected through a leak valve to the high-pressure cell. A rectangular piece of a nickel foil (0.125×6×7 mm, purity 99.99%, Advent) was used as a catalyst. The foil was mounted onto a sapphire sample holder with a SiC plate heated from the rear with a NIR semiconductor laser ($\lambda = 808$ nm) [39]. The undoubted advantage of this heating system is the absence of any hot spots, which might have high catalytic activity. The sample temperature was monitored with a chromel-alumel thermocouple spot-welded directly to the foil edge. The GC analysis was made only in the experiment with the propane/oxygen ratio of 9:1 at

680°C using an on-line four-channel micro gas chromatograph (CP-4900, Varian) equipped with thermal conductivity detectors.

3. Results and discussion

Before in situ experiments, a nickel foil catalyst was activated at 750°C in the reaction mixture ($C_3H_8:O_2$ = 9:1, total pressure of 1 mbar, mixture flow of 60 sccm) for 1.5 h in a flow reactor described elsewhere [28]. In full agreement with our previous results [27], the catalyst pretreated in these conditions exhibits the self-sustained oscillations immediately after the heating in the reaction mixture without an induction period. In the present study, the oscillations were observed at 600–700°C for the propane/oxygen molar ratios from 3:1 to 15:1 at 0.5 mbar.

Fig. 1 shows a typical pattern of the reaction rate oscillations. The catalyst was in an inactive state for the most of the time with periodical evolutions of the reaction products: H_2, CO, and H_2O. Mass-spectrometric detection of CO_2, which is one of the possible reaction products, is complicated due to overlapping of the CO_2 cracking signals at m/z = 12, 16, 28, and 44 with the propane cracking pattern. Therefore, the CO_2 yield was not controlled by mass-spectrometry in this study. However, in our previous experiments with isotope-labeled oxygen $^{18}O_2$, the CO_2 yield was observed to be synchronized with H_2O [27]. The MS signals at m/z = 2 (H_2), m/z = 18 (H_2O), m/z = 28 (CO), and m/z = 32 (O_2) oscillate with the period of 1250 s.

CO and H_2O peaks exhibit a similar shape with the characteristic width of approximately 140 s: their evolutions with time are followed by a slow descent to the initial level of the low catalytic activity (Fig. 1). The oscillatory peaks of H_2 have a slightly different shape: the H_2 signal shows a pronounced shoulder, which is followed by a sharp peak with a long tail. Such shape of the H_2 signal indicates that hydrogen might evolve at different stages of the oscillations: during the transition from the inactive state to the active state, during the active state, and during the reverse transition from the active state to the inactive state. Oxygen oscillations have the inverse form: O_2 uptake is observed in the active half-periods. All these data indicate the existence of at least two states of the catalyst surface with the different activities in the propane oxidation.

Fig. 1 shows also that the periodic changes of the product/reactant concentrations are accompanied with the variation of the catalyst temperature. It should be stressed that the sample was heated with a NIR laser working at the fixed power. Therefore, these temperature

oscillations with the peak-to-peak amplitude of more than 20°C cannot be the result of heating artifacts and reflects the chemical reactions occurring on the catalyst surface.
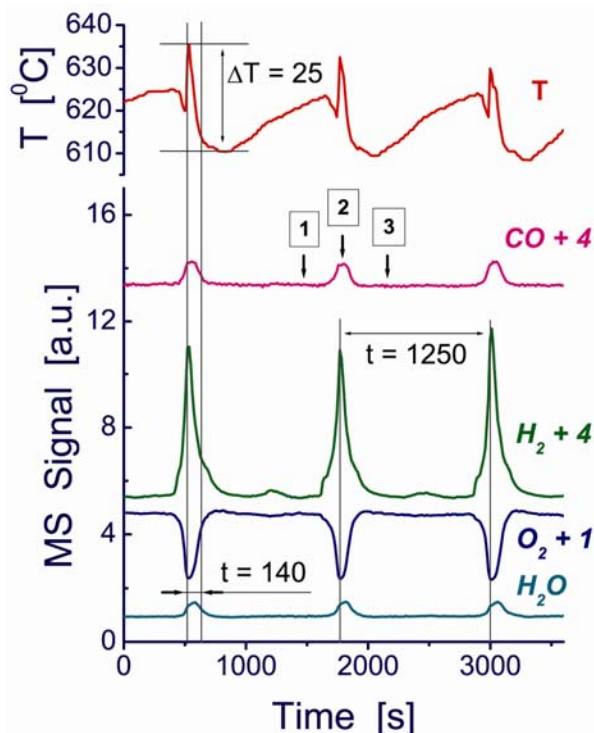

Fig. 1. Self-sustained oscillations in the propane oxidation over the Ni foil at 0.5 mbar with the propane/oxygen ratio of 8:1. The MS signals from H_2, CO, and O_2 are vertically shifted by the factor shown in the legends.

According to the on-line GC measurements, the propane conversion oscillates in the range from 0.5 to 23%. Such products as H_2, CO, CO_2, and propylene were detected by GC. CO selectivity during the active half-periods achieved 98%, while the selectivity towards by-products such as CO_2 and C_3H_6 was only 1–2%. It means that the main route during the active half-periods is the partial oxidation of propane to synthesis gas. During the inactive half-periods, CO selectivity is in the range of 40–60%.

The oscillations of the catalyst temperature show a more complex waveform (Fig. 1). The temperature decrease coincides with the beginning of the oxygen uptake, while the sharp increase of temperature is accompanied with the formation of all products. A maximum temperature corresponds to the highest rate of H_2 evolution. After the maximum, the temperature decays to a minimum, which coincides with almost full termination of all catalytic reactions. The

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gradual temperature rise during the inactive half-period is observed until the next temperature peak. Such complicated behavior of the catalyst temperature and the complex shape of H_2 peaks point that a few chemical processes occur simultaneously over the catalyst surface during the oscillations.

O_2 conversion during the active half-period was not the same for different experiments, varying in the wide range from 15 to 84%, that, however, did not affect the oscillation period. This observation allows us to conclude that the appearance of self-sustained oscillations is not due to the heat and mass transport limitations as it occurs usually in continuous stirred tank reactors for the reactions with strongly non-linear kinetics [2]. It is more probably that the oscillations originate from the change of the chemical state of the catalyst surface. In order to characterize the catalyst surface in the active and inactive states, XPS spectra were taken in situ during the oscillations. The long period and the regular character of oscillations made it possible to acquire several scans of the Ni$2p_{3/2}$ and O$1s$ core-level spectra during the active and inactive half-periods, and then to average these scans to improve the signal-to-noise ratio. The C$1s$ spectra were also acquired; however, the strong signal from gas-phase propane at 285–286 eV completely masks the signal of the carbon-containing adsorbates like $C_xH_yO_z$ (spectra not shown here). Nevertheless, the C$1s$ spectra unambiguously show that neither nickel carbide nor dissolved carbon features at 282–283 eV are observed both in the active state and in the inactive state.

Fig. 2 shows the Ni$2p_{3/2}$ and O$1s$ core-level spectra taken when the system has passed through three characteristic points, which correspond to the inactive and active states. These points are marked as 1, 2, and 3 in Fig. 1. One can see that the binding energy (BE) and the shape of the Ni$2p_{3/2}$ spectra are completely changed when the catalyst surface passes from the inactive to the active state. The spectra from the inactive surface consist of the main component at 854.6 eV with a pronounced high BE shoulder and an additional wide component at 861 eV. The latter feature is a shake-up satellite originating from the multi-electron transitions during the XPS process [40-42]. Typically, the intense shake-up satellites are observed in the spectra of paramagnetic Ni(II) compounds such as NiO, Ni(OH)$_2$, NiAl$_2$O$_4$, etc, whereas the spectra of metallic nickel and diamagnetic Ni(III) compounds do not show shake-up satellite peaks [40-43]. On the other hand, the pronounced high BE shoulder, which is 1.8 eV above the main Ni$2p_{3/2}$ peak, is the unique feature of NiO and is not observed in the Ni$2p_{3/2}$ spectra of nickel hydroxide and nickel aluminate. Moreover, the intensity of this shoulder is highly sensitive to the long-

range structure, and therefore this feature is characteristic of bulk NiO. For instance, it was observed in the spectra of thick NiO films, but not in the spectra of monolayer NiO films [40]. Hence, the Ni$2p_{3/2}$ spectra undoubtedly indicate that during the inactive half-period, the Ni foil surface is covered by a thick film of NiO. It should be stressed that the Ni$2p$ spectra exhibit no nickel carbide and metallic nickel features near 853 eV.
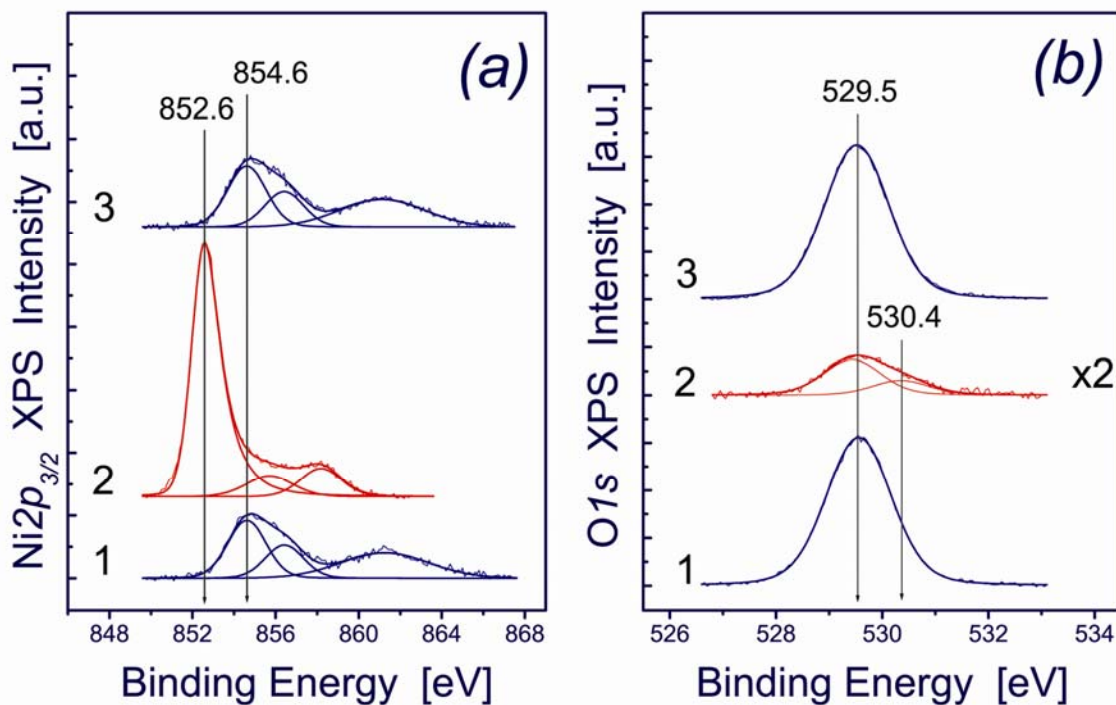

Fig. 2. Ni$2p_{3/2}$ (a) and O$1s$ (b) core-level spectra obtained during the inactive and active half-periods of the oscillations. Spectra 1 and 3 correspond to the inactive state; spectrum 2 corresponds to the active state (see markers in Fig. 1).

In contrast, a narrow component at 852.6 eV, which is the main peak in the Ni$2p_{3/2}$ spectrum from the active surface (Fig. 2a, spectrum 2), is typical of metallic nickel. Two weaker components at 855.7 and 858.2 eV can be associated with energy loss peaks due to Plasmon excitations in metal [42]. It should be noted that some authors suppose that the last, so-called 6 eV satellite, is due to a final-state shake-up process or an initial-state configuration-mixing effect, both the effects being characteristics of metallic Ni [44,45]. Therefore, the transition from the inactive to the active state corresponds to the full reduction of the catalyst surface. Formation of nickel carbide in this case is excluded by the absence of the feature at 282 eV in the C$1s$ spectra.

In good agreement with the transformation of the Ni$2p_{3/2}$ spectra, the corresponding changes were observed in the O$1s$ spectra as shown in Fig. 2b. The O$1s$ spectra of the inactive surface (Fig. 2b, spectrum 1) consist of a single narrow component at 529.5 eV, which can be unambiguously assigned to oxygen in the NiO lattice. This conclusion is based on closeness of the O$1s$ binding energy to literature data for bulk NiO: 529.5–530.2 eV [41,46,47], and of the O/Ni atomic ratio (1.2) to stoichiometric value for the oxide. The absence of higher BE components in the O$1s$ spectrum indicates that the concentration of hydroxyl groups (Ni(OH)$_2$ is characterized by the O$1s$ feature at 531.2–531.6 eV [41,46,47]) in our NiO film is below the XPS detection limit.

The transition to the active state leads to a profound decrease in the O$1s$ intensity (Fig. 2b, spectrum 2). In this case the spectrum can be fitted to two components at 529.4 and 530.4 eV. It should be noted that the O$1s$ binding energies for chemisorbed oxygen and for lattice oxygen of NiO are almost the same with the difference less than 0.3 eV [47]. Therefore, taking into account that the Ni$2p_{3/2}$ spectrum is typical of metallic nickel, the first component at 529.4 eV should be assigned to the chemisorbed oxygen species, while the second component at 530.4 eV could be due to subsurface or dissolved oxygen species. After subsequent transition to the inactive state, the O$1s$ peak at 529.5 eV restores its intensity. According to our rough estimation, the oxygen coverage during the active half-periods is in the range between 0.2 and 0.4 monolayer.
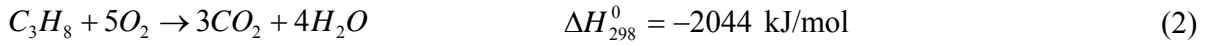
Thus, in situ XPS spectra clearly indicate that during the inactive half-periods, the Ni foil is covered with the NiO layer. However, the presence of small amounts of other oxidic species, such as Ni(OH)$_2$ or Ni$_2$O$_3$, cannot be ruled out. The transition to the active state corresponds to the full reduction of NiO to metallic nickel. It means that during the oscillations, the periodic reduction and oxidation occur within upper layers of the nickel foil. It should be underlined that no Ni^0 features in the Ni$2p$ spectra of the inactive surface were observed even for the photon energy of 1350 eV, when the kinetic energy of the Ni$2p$ photoelectrons was approximately 500 eV. Taking into account that the inelastic mean free path of electrons (λ) with the kinetic energy of 500 eV in NiO is 10.6 Å [48,49] and the XPS information depth is 3λ, the thickness of the NiO layer should exceed 32 Å. Thus, the oscillations originate from the changes of oxidation state of the catalyst bulk.

This conclusion is supported not only by the XPS data, but also by the analysis of the temperature profile (Fig. 1). Indeed, the temperature drop, which occurs simultaneously with the
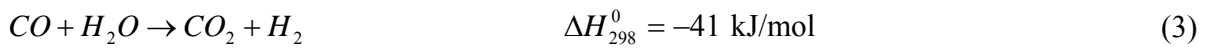
oxygen uptake, indicates that at least one reaction in the system is endothermic. The main reactions, i.e., the partial oxidation of propane to the synthesis gas:
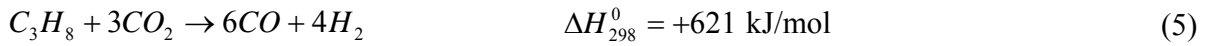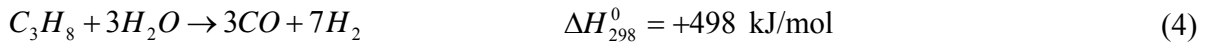
$$C_3H_8 + 1.5O_2 \rightarrow 3CO + 4H_2 \qquad \Delta H^0_{298} = -228 \text{ kJ/mol} \qquad (1)$$
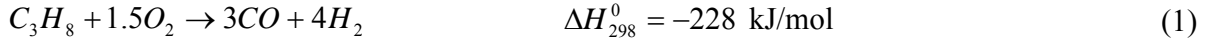
the total oxidation of propane to CO_2 and water:

$$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \qquad \Delta H^0_{298} = -2044 \text{ kJ/mol} \qquad (2)$$

and water-gas-shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \Delta H^0_{298} = -41 \text{ kJ/mol} \qquad (3)$$

which should be also taken into account despite low CO_2 yield, are exothermic [50] and cannot explain the temperature drop. Alternative reactions producing CO and H_2 are steam and CO_2 reforming of propane:

$$C_3H_8 + 3H_2O \rightarrow 3CO + 7H_2 \qquad \Delta H^0_{298} = +498 \text{ kJ/mol} \qquad (4)$$

$$C_3H_8 + 3CO_2 \rightarrow 6CO + 4H_2 \qquad \Delta H^0_{298} = +621 \text{ kJ/mol} \qquad (5)$$

Although both these reactions are endothermic, they still cannot explain the temperature drop. Indeed, being secondary reactions, they are based on the highly exothermic production of CO_2 and H_2O. Moreover, since steam and CO_2 reforming is relatively slow reactions compared to the oxidation reactions (Eqs. (1) and (2)), they cannot strongly affect the catalyst temperature [50]. The most possible reason, explaining the temperature drop, is the stoichiometric reduction of the nickel oxide with propane:

$$3NiO + C_3H_8 \rightarrow 3Ni + 3CO + 4H_2 \qquad \Delta H^0_{298} = +491 \text{ kJ/mol} \qquad (6)$$
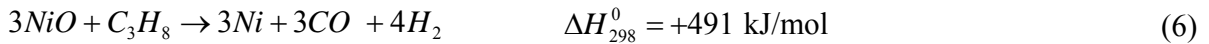
However, in order to provide the observed lowering the catalyst temperature by 25°C (Fig. 1), a reasonably thick oxide layer should react with propane. Subsequent slow increasing the catalyst temperature during the inactive half-periods can be due to the exothermic oxidation:

$$Ni + 0.5O_2 \rightarrow NiO \qquad \Delta H^0_{298} = -240 \text{ kJ/mol} \qquad (7)$$
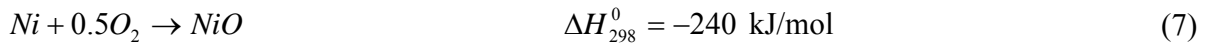
of deeper and deeper nickel layers.

Summarizing the presented data, we can conclude that in spite of strong restructuring of the nickel surface during the induction period [27], the oscillation mechanism of the propane oxidation over Ni cannot be explained in terms of the reconstruction model, but originates from

the periodic oxidation and reduction of the surface and subsurface layers of the catalyst. The absence of the *C1s* features from nickel carbide or from dissolved carbon allows us also to exclude the carbon model.

To the best of our knowledge, this work is the first direct experimental evidence of the redox mechanism of the self-sustained oscillation in the oxidation of light alkanes over transition metals. The oxide model was earlier proposed by Sales, Turner and Maple (STM) for the oscillations in the CO oxidation over Pt, Pd, and Ir [31]. The main feature of the STM model is the formation of surface oxide species which block the surface adsorption sites. The slow oxidation followed by the reduction of the metal surface layer induces transitions between two branches of the Langmuir–Hinshelwood reaction mechanism inducing the oscillations [31]. In contrast with the STM model, the oscillations in the propane oxidation over nickel are controlled by the reversible bulk oxidation of Ni to NiO. According to GC measurements, the switching between the metallic surface and the oxide shows a significant decrease in catalytic activity. This, together with the variation in the product distribution observed for the active and inactive half-periods, suggests the changes in the reaction mechanisms. We guess that the Langmuir–Hinshelwood mechanism is realized for the propane oxidation over the metallic Ni surface, whereas the reaction over NiO follows the Mars–van Krevelen mechanism where the oxidation of propane with the NiO lattice oxygen is coupled with subsequent reoxidation of the reduced surface by oxygen from the gas phase [51]. Considering the propane oxidation as a case reaction, we suppose that the rate oscillations in the oxidation of other light alkanes over transition metals (like Ni, Co, etc) proceed through the similar mechanism.

A similar mechanism was recently proposed by Hendriksen and coworkers [52,53] for the oscillations in the rate of CO oxidation over Pt and Pd observed under atmospheric conditions. The authors supposed that the high-pressure reaction oscillations were not due to the bistability in the Langmuir–Hinshelwood kinetics, but arose from the periodic switching between the low-reactive metallic surface and the high-reactive oxide surface. The reaction over metallic surface follows the Langmuir–Hinshelwood mechanism, whereas metal-to-oxide transition changes the reaction to the Mars–van Krevelen mechanism. It seems that the STM mechanism, as well as the so-called subsurface oxygen mechanism [54] based on an assumption that the oscillation in catalytic activity is caused by the variation of oxygen sticking probability under the influence of subsurface oxygen, is realized at vacuum conditions only. At elevated pressures the

self-sustained oscillations in catalytic oxidation reactions over transition metals are more probably to follow the redox mechanism based on the reversible bulk oxidation of the catalyst.

The reasons causing the transition between the active and inactive states or between metallic Ni and NiO are not clear yet. One of the possible reasons was discussed in the cited paper by Hendriksen et al. [53], who proposed that formation and annealing of the surface atomic steps is a driving force for reduction–oxidation during oscillations of CO oxidation over Pt under elevated pressures. Using in situ XRD, they identified the processes of smoothening of the metal surface and roughening of the oxide one during inactive and active half-periods of the oscillation, respectively.

One can also suppose that dissolved or subsurface oxygen in metallic nickel and/or defects in NiO play an important role for feedback mechanism. For instance, interconnection between the number of oxygen vacancies and catalytic activity in the CO oxidation was recently reported for the RuO_2 catalysts [55]. It has been shown that completely oxidized polycrystalline ruthenium dioxide (RuO_2 pre-calcined in O_2 at 1073 K) does not exhibit any activity and a long induction period in the feed at 503 K is necessary to activate RuO_2, which then provides 100% conversion of CO. At the same time, in situ XRD reveals no changes in the RuO_2 diffraction pattern before and after the induction period. High activity was explained by the formation of the defects in ruthenium oxide [55].

By analogy with this example, we can speculate that the transition between the active and inactive states proceeds through some transient states, which are similar to a solid solution of oxygen in metallic nickel or to highly defective nickel oxide. Appearance of the defects in NiO can facilitate the heterolytic activation of C–H bond of propane (the key step in the Mars–van Krevelen mechanism) increasing the rate of propane interaction with lattice oxygen. Fast removal of oxygen will reduce NiO to Ni. The solid solution of oxygen in metallic nickel above a critical level can lead to the back transformation of the surface layers to nickel oxide.

4. Summary

The self-sustained oscillations in the propane oxidation over a nickel foil have been studied in situ with the use of ambient-pressure XPS coupled with on-line mass-spectrometry and gas chromatography. According to the Ni*2p* and O*1s* core-level spectra of the catalyst surface, during the active half-period nickel in the surface and subsurface layers is in the metallic state, whereas during the inactive half-periods the catalysis surface is covered with a layer of

NiO with a thickness of at least 3 nm. GC measurements showed that the activity of metallic nickel is approximately 40-fold higher than that of NiO. We suggest that propane oxidation over the metallic Ni surface occurs according to the Langmuir–Hinshelwood mechanism and the main reaction route is the partial propane oxidation to CO and H_2, whereas the reaction over NiO follows the Mars–van Krevelen mechanism, not only CO, but also CO_2 and propylene being detected among the products of propane oxidation in this case. Hence, the reversible reduction/oxidation of the catalyst bulk affects strongly the catalytic properties of nickel and even changes the mechanism of propane oxidation.

ACKNOWLEDGMENT

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