

Full title: *In Situ* Study of Self-Sustained Oscillations in Propane Oxidation and Propane Steam Reforming with Oxygen over Nickel

Short title: *In Situ* Study of Self-Sustained Oscillations...

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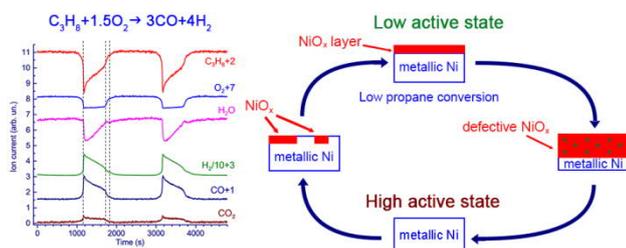
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Abstract

Self-sustained reaction rate oscillations in the oxidation of propane and in the propane steam reforming with oxygen over nickel foil have been studied *in situ* by near-ambient pressure X-ray photoelectron spectroscopy and mass-spectrometry. It was found that regular relaxation-type oscillations in both reactions proceed under similar conditions. In the former case, the peaks of CO, CO₂, H₂, and H₂O were detected by mass-spectrometry as gas-phase products. In contrast, in the latter case, after addition of water to the reaction feed, the mass-spectrometric signal of water decreased simultaneously with the signals of O₂ and C₃H₈, whereas the signals of CO, CO₂, and H₂ increased. It means that in the presence of water in the reaction feed, the propane steam reforming proceeds with a significant rate. In both cases, the oscillations arise due to spontaneous oxidation and reduction of the catalyst. According to the Ni2p and O1s core-level

spectra measured *in situ*, the high-active catalyst surface is represented by nickel in the metallic state, and the transition to the low-active state is accompanied by the growth of a NiO film on the catalyst surface. The oscillations in the gas phase are accompanied by oscillations in the catalyst temperature, which reflects proceeding endothermic and exothermic processes. An oscillatory mechanism, which can be common for oxidative catalytic reactions over transitional metals, is discussed.

Graphical abstract



1 Introduction

Since the discovery of self-sustained reaction rate oscillations in the catalytic oxidation of CO on platinum metals in 1970 [1], a huge amount of scientific researches was devoted to the study of this peculiar phenomenon. This also initiated a search for other oscillating heterogeneous reactions. As a result, kinetic oscillations have been discovered in a wide range of catalytic reactions, including the oxidation of CO, H₂, or various organic compounds, the hydrogenation of CO and hydrocarbons, NO reduction, and N₂O decomposition [2-4]. To date, the oscillatory behavior was observed in approximately 40 heterogeneous catalytic reactions in a wide pressure range from ultra-high vacuum to atmospheric pressure over different types of catalysts. Because of practical importance, in the last decade, more attention was paid to studying the oscillations in the catalytic oxidation of CO, methane, ethane, and propane over transitional metals [5-18]. This provided new insight into the chemistry and structure of catalysts under reaction conditions and allowed understanding the main causes of activation and deactivation of the catalysts.

Here we present the first results of our mechanistic study of the self-sustained oscillations in another reaction — the propane steam reforming with added oxygen over nickel foil. The oscillations in this catalytic system were observed in 2005 [19]; however, the oscillatory mechanism was not investigated. Because the oscillations in the propane steam reforming with added oxygen were observed under the similar conditions as oscillations in the oxidation of propane, we compared the oscillatory kinetics in these reactions and then performed an *in situ* study of both reactions by near-ambient pressure X-ray photoelectron spectroscopy (NAP XPS) coupled with mass-spectrometry (MS). This allowed us to observe the oscillations of products and reactants in the gas phase in real time by mass-spectrometry, oscillations in the catalyst temperature and to run the NAP XPS analysis of the catalyst surface in the moments when the catalyst was in the low-active state or in the high-active state. Simultaneously, we studied oscillations in the catalyst temperature that reflect proceeding endothermic and exothermic processes. The obtained data made it possible to find a correlation between the chemical state and the activity of the catalyst and to elucidate the oscillatory mechanism.

2 Experimental section

The *in situ* experiments were performed at the Innovative Station for In Situ Spectroscopy at the synchrotron radiation facility BESSY II (Berlin, Germany). The construction of the station was described in detail elsewhere [20]. In short, the station was equipped with an electron energy analyzer (PHOIBOS-150, SPECS Surface Nano Analysis GmbH), a gas cell, and a system of electron lenses with three differential pumping stages. The high brilliance of the synchrotron radiation combined with a short travel-length of photoelectrons through a “high pressure” zone in the gas cell allowed us to obtain high-quality core-level spectra under flow conditions at pressures up to 1 mbar with the time resolution of approximately 100 s. The station was also equipped with a MKS 121A baratron (MKS Instruments Inc.), a quadrupole mass spectrometer (Prizma, Pfeiffer Vacuum GmbH) connected through a leak valve to the gas cell, and mass-flow controllers (Bronkhorst High-Tech BV).

In all the experiments, rectangular pieces of a 0.125-mm thick nickel foil (purity 99.99%, Advent Research Materials Ltd.) were used as a catalyst. A sample 9×9 mm in size was mounted on a sapphire sample holder between a SiC plate and a stainless steel plate, which had a hole of 8 mm in diameter for measuring the core-level spectra of the catalyst surface. The sample was heated from the rear through the SiC plate with a near-infrared semiconductor laser ($\lambda = 808$ nm). The sample temperature was monitored with a K-type thermocouple spot-welded directly to the foil edge. During the *in situ* experiments, the total pressure in the gas cell was kept at a constant level of 0.5 mbar using a special automatic pumping system. The flows of propane, oxygen, and water were regulated separately.

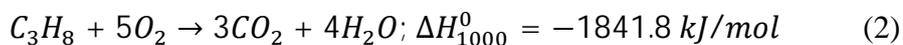
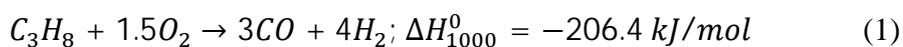
All the photoelectron spectra were collected at the normal emission at the constant pass energy of 10 eV; their intensities were normalized to the ring current. The Ni $2p_{3/2}$, O1s, and C1s core-level spectra were obtained with photon energies of 1050, 730, and 485 eV, respectively, that provided the same kinetic energy (approximately 200 eV) for each region and, correspondingly, the same analysis depth of approximately 1.7 nm. The positions of the photoelectron peaks on the binding energy scale were referenced to the Fermi edge of nickel in the metallic state. All spectra were analyzed using the CasaXPS software. The procedure of curve-fit analysis has been described in detail elsewhere [15].

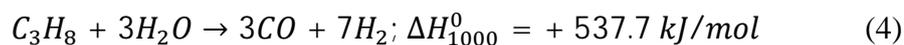
3 Results and discussion

Our investigations were started from the *in situ* study of the self-sustained oscillations in the oxidation of propane by molecular oxygen. Recently, we showed [11, 15, 17] that regular oscillations of the propane oxidation rate arose under oxygen-deficient conditions, when the molar ratio of propane to oxygen ranged between 15:1 and 1:1. The period of oscillations varied from several to tens of minutes, which is suitable for the NAP XPS analysis of the catalyst surface. On the basis of these findings, the experiment was carried out as follows. First, the nickel foil used as a catalyst was fixed on the sample-holder set to the gas cell, and then the flows of propane and oxygen were adjusted. The flow of propane was 5.9 sccm, and the flow of

oxygen was 0.65 sccm, which provided the C₃H₈:O₂ molar ratio of 9:1. Because the catalyst was pre-activated and it had demonstrated the oscillatory behavior [11, 15], the self-sustained oscillations arose without any induction period, immediately after heating the foil to approximately 600 °C.

A typical pattern of the reaction rate oscillations in the catalytic oxidation of propane observed by MS is shown in Figure 1 (Stage I). One can see that these are the relaxation-type oscillations, which can be characterized with fast transitions (jump up and jump down) between low-active and high-active states. The catalyst stays in the low-active state for some time with periodic evolutions of the reaction products: H₂, CO, and H₂O. Mass-spectrometric detection of CO₂, which is one of possible reaction products, is complicated because of overlapping of the CO₂ cracking signals at m/z = 12, 16, 28, and 44 with the propane cracking pattern. As a result, the oscillations of CO₂ signals were inexpressive under the conditions used. However, in our previous experiments with isotope-labeled oxygen ¹⁸O₂, the CO₂ yield was clearly observed to be synchronous with H₂O [19]. Such product distribution indicates that there proceed both the partial oxidation of propane to CO and H₂ (1) and the total oxidation of propane to CO₂ and H₂O (2). In our previous study with on line gas chromatography [15], we have shown that the selectivity toward CO achieves 98% when the catalyst is in the high-active state. The transition to the low-active state is accompanied by decreasing the selectivity toward CO to 60-65%. In the latter case, the formation of propylene and CO₂ was also observed with selectivity near 25-30% and 11-14%, respectively. Hence, the partial oxidation is the main reaction route, at least when the catalyst is in the high-active state. This conclusion is supported by the lower intensity of the CO₂ peaks in comparison with the intensity of the CO peaks (Figure 1).





The values of ΔH_{1000}^0 were calculated using the temperature dependence of heat capacity according the equation $C_p = a + bT + c/T^2$, where a, b, and c were taken from the reference book [21].

As seen from Figure 1, the oscillations of the O₂ signal are similar to the square wave while the oscillations of the other MS signals have a more complex shape. Indeed, the fast transition from the low-active state to the high-active state leads to a sharp increase in the partial pressures of CO, CO₂, H₂O, and H₂. After that, the yields of CO, CO₂, and H₂ decrease slowly, whereas the H₂O yield increases slightly after a small decrease. This means that some slow transformation of the nickel surface occurs when the catalyst is in the high-active state. During the transition to the low-active state, the MS signals of products are gradually reduced to zero.

The oscillations in the gas phase are accompanied by the oscillations in the catalyst temperature with the amplitude about 25 °C. The transition to the high-active state is accompanied by an increase in the temperature, which confirms that there proceed exothermic reactions such as the partial (1) and total (2) oxidation of propane over the catalyst in the high-active state. After the transition to the low-active state, the catalyst temperature starts to decrease because of the heat transfer into the gas phase.

The oscillations do not disappear after addition of water to the reaction feed. The main change in the oscillations in this case can be observed for the MS signal at m/z = 18 (H₂O): their shape inverts, indicating that water reacts with propane when the catalyst is in the high-active state (Figure 1, Stage II). Because the strong peaks of CO, CO₂, and H₂ appear synchronously with the uptake of C₃H₈, O₂, and H₂O, we can speculate that, in addition to the partial oxidation (1), the steam reforming of propane (Eq. 3 and 4) also proceeds over the catalyst in the high-active state. A comparison of the CO and O₂ profiles in Stage I and Stage II indicates that the steam reforming of propane provides approximately 30% of the CO yield. The contribution of

secondary reactions, such as the water-gas-shift reaction and the oxidation of CO and H₂, to the overall catalytic process is negligible.

In contrast, after switching off the O₂ flow, the oscillations disappear immediately, and the rate of all catalytic reactions drops to zero (Figure 1, Stage III). It is very likely that the catalyst passes to some low-active state. This transition is reversible: when we stopped the H₂O flow and set the O₂ flow, the self-sustained oscillations with almost the same shape and period appeared after some delay (Figure 1, Stage IV).

It should be noted that the oscillations of products and reactants in the gas phase in the propane steam reforming with oxygen are accompanied by oscillations in the catalyst temperature as well. In comparison with the temperature oscillations observed in the oxidation of propane, the temperature oscillations decrease in amplitude in the presence of water in the reaction feed. This effect is due to both the endothermic steam reforming and the exothermic partial oxidation of propane, which proceed simultaneously over the catalyst in the high-active state. Moreover, the shape of oscillations changes significantly: one can see the extremely narrow peaks in the catalyst temperature when the catalyst passes from the low-active state to the high-active state. Because there are no corresponding peaks in the O₂ and H₂O signals, this effect may be associated with some changes in the chemical state of the catalyst.

It is very important that the addition of water only slightly changes the period of oscillations. In the oxidation of propane (without water in the feed) the MS signals at $m/z = 2$ (H₂), $m/z = 18$ (H₂O), $m/z = 28$ (CO), $m/z = 32$ (O₂), and $m/z = 44$ (CO₂) oscillate with the period of 1300 s (Figure 1). After adding water, the period increases to approximately 2000 s. In both cases, this is enough for the *in situ* NAP XPS analysis of the catalyst state, and we managed to obtain the Ni2p_{3/2} and O1s high-quality spectra of the catalyst in the high-active state and in the low-active state (the time-scale of the spectra was near 40 and 20 s, respectively). The spectra are presented in Figure 2. In full agreement with our previous studies [11, 15, 17], the self-sustained oscillations in the oxidation of propane (without water in the reaction feed) are

accompanied by periodic oxidation and reduction of nickel. Undoubtedly, the Ni $2p_{3/2}$ spectrum of the catalyst in the high-active state is typical of nickel in the metallic state, whereas the Ni $2p_{3/2}$ spectrum of the catalyst in the low-active state is typical of bulk NiO.

Indeed, the spectrum of the high-active state contains the intense peak at 852.6 eV and two low-intense satellites at 855.8 and 858.1 eV. A similar Ni $2p_{3/2}$ spectrum was obtained for the cleaned Ni foil (Figure 2). In the latter case, the spectrum also consists of the main peak at 852.6 eV and satellites at 856.0 and 858.6 eV. Most researchers suppose that such a line-shape is due to final-state effects, which result from the created hole and the excited electron [22, 23]. For example, Hüfner [24] attributed the satellite at ~6 eV above the main emission peak in the Ni $2p_{3/2}$ spectrum (at 852.6 eV) to an electron configuration with two holes $c3d^94s^2$ ('c' here denotes a core hole) in the final state. In fact, the origin of these satellites is still not clear (see Ref. [23] and references therein) and could be attributed to one-electron or multi-electron excitations, or to the hybridization between d , p , and s atomic orbitals [25, 26]. It should be noted that the position and intensity of these satellites are sensitive to the electronic state of nickel atoms and, as a result, depend on a Ni nanoparticle size and a thickness of Ni films [22, 23]. Moreover, Ar⁺-ion bombardment of supported Ni clusters, which usually provides the formation of defects, leads to a shift in the satellites to a higher binding energy and to a decrease in their intensity [23]. From this point of view, the difference in the satellite structure of the Ni $2p_{3/2}$ spectra of the catalyst in the high-active state and the cleaned Ni foil may be explained with the fact that the catalyst in this state contains a larger number of defects. This hypothesis agrees well with our previous study [15] where we observed the formation of a rough and porous structure over the catalyst surface after appearing the self-sustained oscillations in the oxidation of propane. This structure is formed as a result of periodic reduction and oxidation of nickel and may contain surface and bulk defects.

The transition of the catalyst to the low-active state is accompanied by strong changes in the Ni $2p_{3/2}$ spectrum (Figure 2). The spectrum consists of 5 peaks at 853.9, 855.4, 860.9, 864.1,

and 866.5 eV. The shift of the Ni2p_{3/2} spectrum to higher binding energies points to the oxidation of nickel. The presence of the intense satellite at 6-7 eV above the main emission peak in the Ni2p_{3/2} spectrum unambiguously indicates that nickel in this case is in the Ni²⁺ state; this satellite is only observed in the spectra of Ni(II) compounds such as NiO, Ni(OH)₂, NiSiO₃, and NiAl₂O₄ [27-29]. However, the presence of the other intense satellite (at 1.5 eV above the lowest peak) is typical of only NiO. Moreover, the intensity of this peak is highly sensitive to the long-range ordering and, hence, it is the most characteristic feature of bulk NiO. Indeed, this feature is typically observed in the spectra of thick NiO films and is not observed in the spectra of monolayer NiO films [30]. The absence of photoemission signals at 852.6 eV indicates that the transition to the low-active state is accompanied by complete oxidation of Ni in the upper layers of the catalyst. At the same time, the Ni2p_{3/2} spectrum of the catalyst in the low-active state is slightly different from the spectrum of the NiO film, which is also presented in Figure 2 for comparison. The main distinctions here are the small shift of the satellites by 0.1–0.2 eV, the increase of 14% in the relative intensity of the satellite at 855.4 eV, and the increase in the peak widths. These minor differences suggest that the low-active state is similar to bulk NiO but is probably defect-rich and thus lacks the extended long-range order.

The periodic oxidation and reduction of nickel is also supported by the O1s spectra observed *in situ*. For example, when the catalyst is in the low-active state, its O1s spectrum exhibits a strong peak at 529.4 eV with a weak shoulder at 531.4 eV (Figure 2). The first peak unquestionably corresponds to O²⁻ oxygen species in the NiO lattice. The origin of the second peak is not so obvious despite the fact that it is often observed in the spectra of nickel oxide. Some authors assign this peak to oxygen atoms in the positions adjacent to Ni vacancies within the oxide structure or even attribute this peak to Ni₂O₃ (see Ref. [31] and references therein). Indeed, the formation of the cationic vacancy must be accompanied by changes in the chemical state of adjacent oxygen atoms [32] and by an increase in their O1s binding energy [33]. Therefore, we attributed the O1s peaks at 529.4 and 531.4 eV (Fig. 2) to the O²⁻ oxygen species

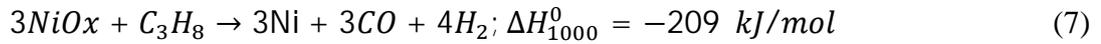
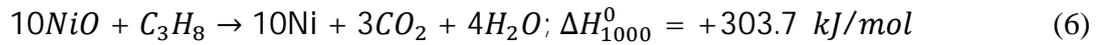
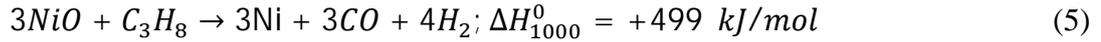
in the NiO lattice and to some defects such as $O^{2-}-Ni^{3+}-O^{1-}-\square$ (\square is a cationic vacancy), respectively. Of course, the presence of OH-groups, which are also characterized by a similar O1s binding energy, cannot be excluded either. According to our XPS study [15], the O1s spectra of the thick NiO film and bulk $Ni(OH)_2$ contain strong peaks at 529.6 and 531.4 eV, respectively.

The transition to the high-active state is accompanied by a significant decrease in the intensity of the O1s spectrum, which indicates the reduction of NiO to metallic Ni. The spectrum consists of two peaks at 529.4 and 531.4 eV (Figure 2). Taking into account the shape of the $Ni2p_{3/2}$ spectrum, these peaks can be attributed mainly to atomic oxygen and hydroxyl groups adsorbed on metallic nickel. The presence of a small amount of NiO cannot be ruled out either. Unfortunately, the O1s binding energies of chemisorbed oxygen and oxygen in the lattice of NiO are almost the same, differing by no more than 0.3 eV [34, 35]. Besides, the O1s binding energy of chemisorbed oxygen depends on coverage. As shown by Öfner and Zaera [34], oxygen atoms in the low-coverage (2×1) structure are characterized by the O1s peak at 529.7 eV, whereas oxygen atoms in the high-coverage (3×1) structure and in the NiO film are characterized by the O1s peak at 529.4 eV. OH- groups adsorbed on Ni(110) are characterized by the O1s peak at 531.6 eV [36]. It should be noted that the C1s spectra acquired in the moments of high and low conversion of propane do not contain any features in the range between 281 and 290 eV. This means that adsorbed propane molecules immediately dissociate and react with oxygen over the catalyst surface both in the low-active state and in the high-active state.

The addition of water to the reaction feed does not affect the character of changes in the $Ni2p_{3/2}$ and O1s spectra. Moreover, the $Ni2p_{3/2}$ spectra of the high-active and low-active states are almost identical to the spectra observed without water. There were no remarkable changes in the O1s spectrum of the low-active state as well: the spectrum consisted of a strong peak at 529.4 eV with a weak shoulder at 531.4 eV. The main difference was observed in the O1s spectrum of the high-active state. The spectrum contained four peaks at 529.4, 530.7, 531.4, and 532.4 eV.

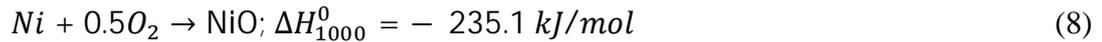
Nevertheless, the peaks at 529.4 and 531.4 eV can be attributed to oxygen atoms and hydroxyl groups adsorbed on metallic nickel, respectively; while the peak at 532.4 eV undoubtedly corresponds to adsorbed water [36]. The detection of adsorbed water agrees well with the MS data presented in Figure 1, which indicate that the concentration of water in the gas phase increases approximately fivefold after the addition of water to the reaction feed. The origin of the peak at 530.7 eV is not evident. We attribute this peak to oxygen atoms dissolved in the near surface layers of nickel. Usually, the dissolved oxygen species are characterized by an O1s binding energy that is higher than that of chemisorbed oxygen species. For example, the O1s binding energy of oxygen adsorbed on Pd(111) is 529.2 eV, whereas the O1s binding energy of subsurface or dissolved oxygen species is 529.7 eV [37].

Hence, these *in situ* NAP XPS data indicate that the self-sustained oscillations in the steam reforming of propane with oxygen also originate from the periodic reduction and oxidation of nickel. An extra argument to support this hypothesis can be obtained from the analysis of the temperature oscillations presented in Figure 3. One can see that the transition from the low-active state to the high-active state starts from the sharp peak of the catalyst temperature. This peak is accompanied by a sharp increase in the MS signals of products (CO, CO₂, and H₂) and, correspondingly, by a sharp decrease in the MS signal of propane. In contrast, this effect is not observed in the MS signals of O₂ and H₂O. This means that the transition from the low-active state to the high-active state occurs due to some exothermic reactions in which O₂ and H₂O are not involved. These reactions cannot be the reduction of stoichiometric NiO by propane to CO and H₂ (5) or to CO₂ and H₂O (6) because they are endothermic. We can speculate that this is the reduction of high-defect nickel oxide (NiO_x) by propane. Indeed, this reaction is exothermic: it is necessary first to consume energy for the formation of NiO_x from perfect NiO. According to calculations from first principles [38], the formation energy of a nickel vacancy in bulk NiO is approximately 236 kJ/mol. This means that the reduction of defect-rich nickel oxide by propane is an exothermic process (7).



Summarizing, we can suggest the following tentative model to explain the appearance of self-sustained oscillations in the oxidation of propane over nickel (Figure 4). The cycle starts with a thick NiO layer, which covers Ni foil. This is the low-active state and the rate of all catalytic reactions is low. The catalyst temperature is approximately equal to a minimal value that is determined by the heater used. Then, some defects in the NiO film are formed under the reaction conditions, and their number gradually increases. When the concentration of these defects achieves a certain level, the defect-rich nickel oxide is fast reduced by propane and the catalyst passes to the high-active state. This is not a catalytic process, and we detected the appearance of the products in the gas phase without an uptake of O₂ and H₂O. As discussed above, the reduction of NiO_x to metallic Ni is an exothermic process and, as a result, the transition from the low-active state to the high-active state is accompanied by a sharp increase in the catalyst temperature. Upon the reduction of nickel oxide, the temperature drops to the minimum because the reduction of perfect NiO is an exothermic process and then increases monotonously because of the partial oxidation of propane. Despite the increasing the catalyst temperature, the conversion of propane decreases slowly, indicating the catalyst deactivation. Most probably, the deactivation proceeds as dissolution of oxygen in nickel or formation of surface oxide clusters that block the catalyst surface [39]. The accumulation of oxygen in the near-surface layers of nickel initiates the reverse transition from the high-active state to the low-active state (Ni → NiO) and a thin NiO film is formed on the Ni foil surface at first. Because the activity of NiO is 20-fold lower than the activity of metallic Ni in the oxidation of propane [15], after the formation of the NiO film, the catalyst temperature decreases sharply owing to the

formation of defects in the NiO lattice. The following increase in the catalyst temperature can be attributed to the further oxidation of Ni through the exothermic process (Eq. 8) and the formation of a thick NiO film. This process slows down with increasing the film thickness because the oxygen diffusion is an activated process [38]. As a result, the catalyst temperature achieves its minimum again.



According to our experimental data, the same oscillatory mechanism is implemented in the propane steam reforming with added oxygen over nickel. This means that the driving force for these self-sustained reaction-rate oscillations is also the reversible bulk oxidation of the catalyst. Water slowly reacts with NiO and cannot initiate strong changes in the catalyst state. On the surface of metallic Ni, water can adsorb and then dissociate and react with adsorbed carbon-containing species. However, oxygen is more active than water and the dominant catalytic reaction is the oxidation of propane while the propane steam reforming is a subordinate process.

Therefore, the mechanism based on the formation and decomposition of high-defect nickel oxide film over the catalyst surface explains the temperature oscillations and, moreover, it predicts a possibility of the fast transition from the low-active state to the high-active state. Indeed, NiO_x is metastable and energy-saturated and can spontaneously decompose to metallic nickel with an energy release. This process is exothermic and involves many upper layers of the catalysts. As a result, the transition from the low-active state to the high-active state is accompanied by the sharp temperature peak.

Because the type of reactants does not directly affect the scenario of the oscillatory behavior described above, this oscillatory mechanism can be realized in other catalytic reactions in which molecular oxygen is used as an oxidant. At least the self-sustained oscillations that

were observed in the oxidation of methane [18], ethane [40], and CO [41] over Ni most likely proceed through a similar mechanism.

4 Conclusions

Self-sustained reaction rate oscillations arise in oxygen-deficient conditions in the oxidation of propane and in the propane steam reforming with added oxygen. In both cases, the main reaction is the partial oxidation of propane to CO. Self-sustained oscillations in the propane steam reforming without oxygen are not observed. The oscillations originate from the spontaneous oxidation and reduction of nickel. These are the relaxation-type oscillations. The oscillations of products and reactants in the gas phase are accompanied by the oscillations of the catalyst temperature. Because the oxidation of propane is exothermic, the catalyst may heat up to 25 °C when it is in the high-active state. Ni in the metallic state is more active than NiO, and the high-active state is attributed to metallic Ni. The transition from the high-active state to the low-active state proceeds via two stages. First, a thin NiO film grows over the catalyst surface, leading to a slow decrease in the yield of products. Then, the thickness of the NiO film increases significantly, which is accompanied by a fast decrease in the propane conversion. The NiO film contains a great number of point defects, which is confirmed by NAP XPS. The defects are formed under reaction conditions and when their concentration achieves a critical level, a fast reduction of high-defect NiO by propane proceeds leading to the transition of the catalyst from the low-active state to the high-active state. This process is similar to a “surface explosion” and is accompanied by a sharp increase of the catalyst temperature. This scenario of oscillatory behavior can be realized in other catalytic reactions, in which molecular oxygen is used as an oxidant.

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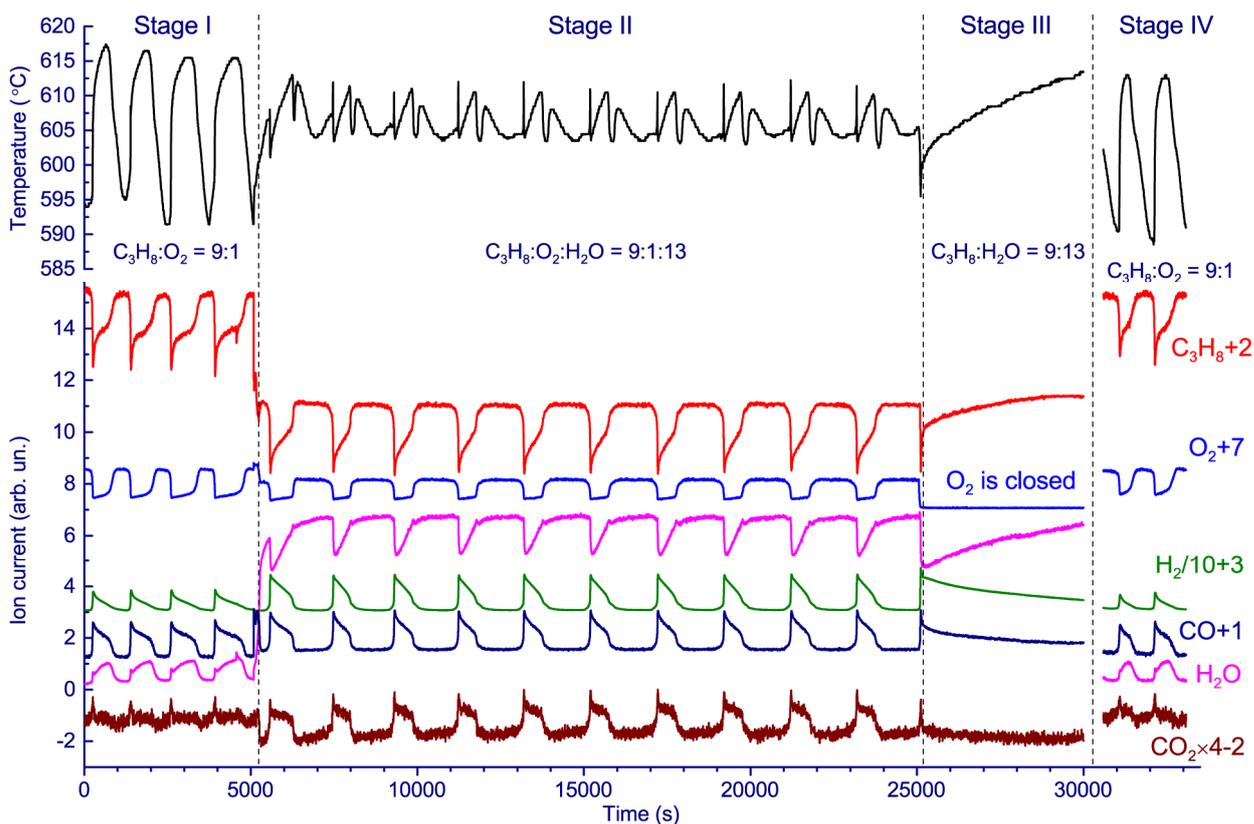


Figure 1. Oscillatory behavior in the oxidation and steam reforming of propane over Ni foil. Total pressure in the gas cell is 0.5 mbar. The molar ratios of the feed for each stage are presented the legends. MS signals of reactants and products are vertically shifted by factors shown in the legends. Additionally, the H₂ signal is divided by 3, the CO₂ signal is multiplied by 4.

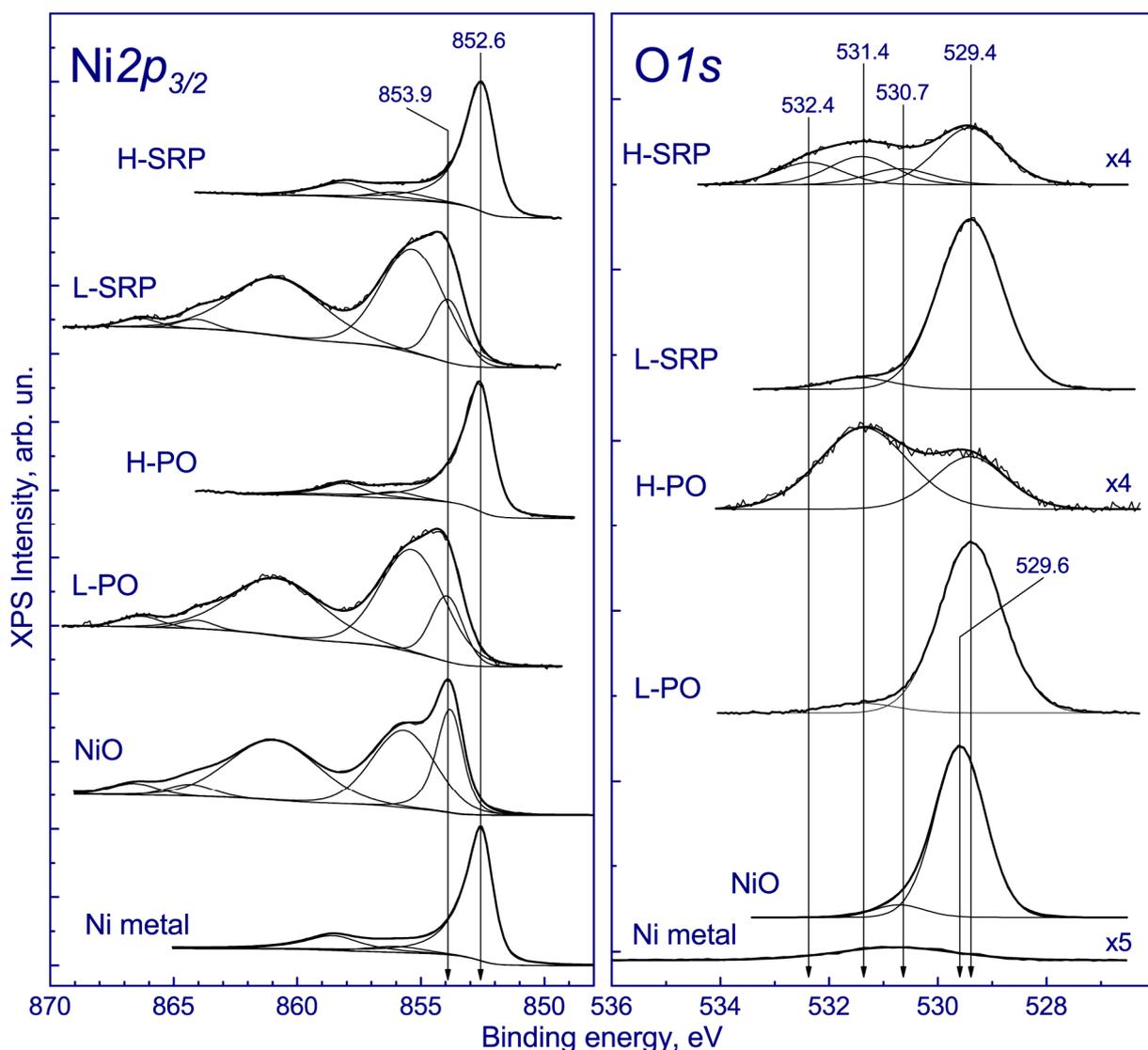


Figure 2. Ni $2p_{3/2}$ and O $1s$ core-level spectra of the catalyst in the high-active state (H) and in the low-active state (L) obtained *in situ* during self-sustained oscillations in the propane oxidation (PO) and in the steam reforming of propane with oxygen (SRP) simultaneously with the MS data presented in Fig. 1. The spectra of cleaned Ni foil (Ni metal) and a NiO film grown by a treatment of the cleaned Ni foil in O $_2$ at 1 bar for 10 min at 300 °C (NiO) are shown for comparison; the spectra were acquired at room temperature in UHV. The Ni foil was cleaned by repeated cycles of Ar $^+$ -ion sputtering (2 keV, 20 μ A, and 20 min) and subsequent annealing in vacuum at 600 °C.

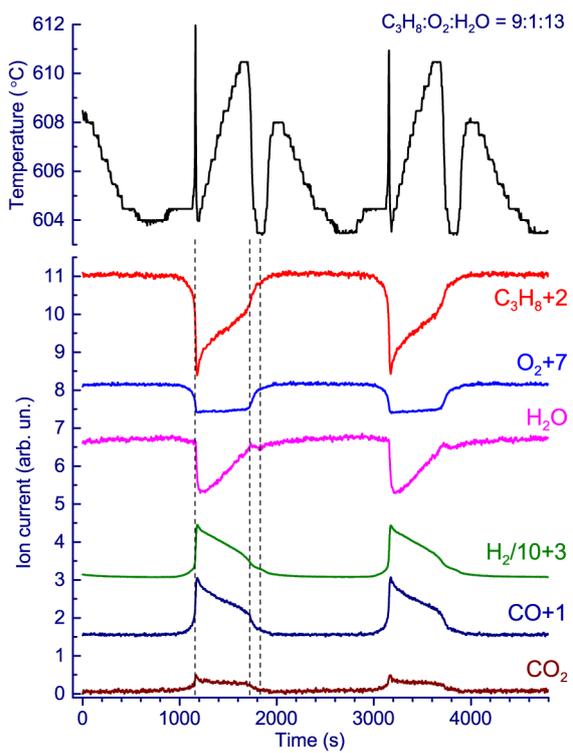


Figure 3. Oscillations of the catalyst temperature (upper panel) and oscillations of products and reactants in the gas phase (lower panel) observed in the propane steam reforming with added oxygen over Ni foil.

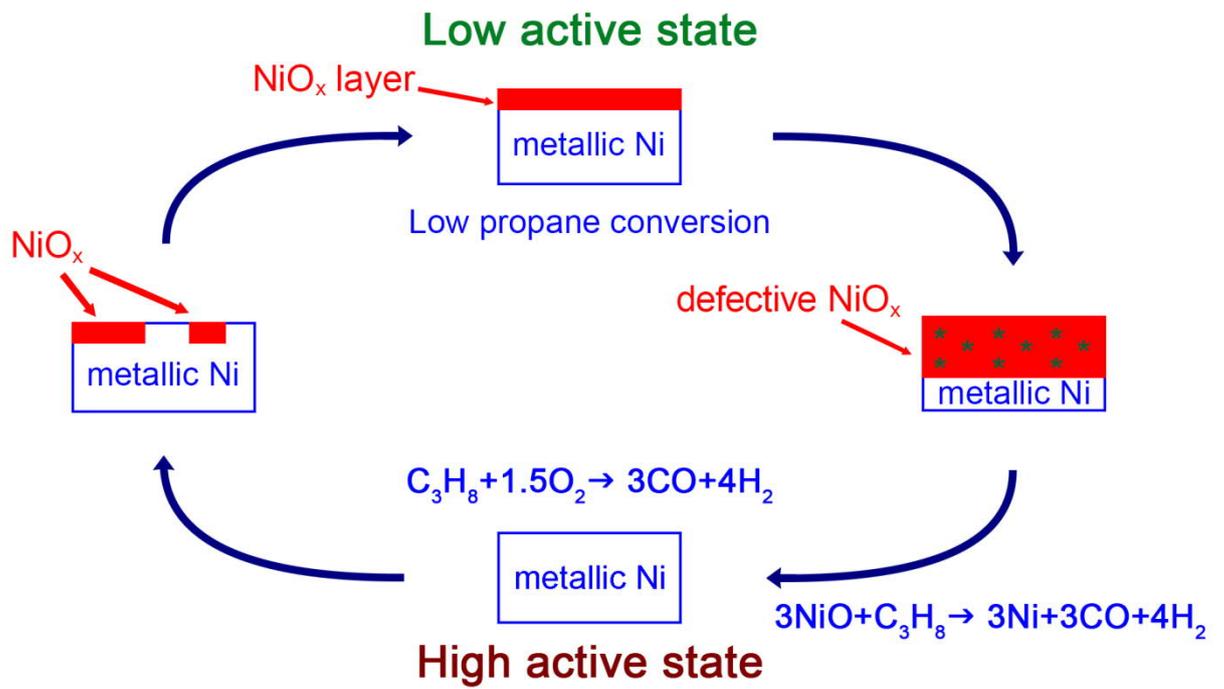


Figure 4. Oscillatory mechanism in the catalytic oxidation of propane over nickel.

Keywords: Heterogeneous catalysis · Non-linearity · Oscillations · XPS