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The origin of self-sustained reaction-rate oscillations in the oxidation of methane over nickel: an *operando* XRD and mass spectrometry study

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The self-sustained kinetic oscillations in the catalytic oxidation of methane over Ni foil have been studied at atmospheric pressure using an X-ray diffraction technique and mass spectrometry. It has been shown that the regular reaction-rate oscillations appear under oxygen-deficient conditions and the period of oscillations varies between approximately 200 and 4000 s. The *operando* measurements have revealed a higher activity of metallic Ni in the reaction than NiO oxide and have unambiguously showed that the oscillations arise due to the reversible bulk oxidation of Ni to NiO.

Self-sustained kinetic oscillations are often observed in different heterogeneous catalytic reactions under certain conditions.^{1–3} Depending on the feedback mechanism, chaotic, sinusoidal or harmonic oscillations can arise. Furthermore, the relaxation-type oscillations, which can be described as a fast evolution (jump up and jump down) between low-active and high-active states, have been reported for oxidation of hydrocarbons. For example, relaxation-type oscillations have been observed in our study of the propane oxidation over Ni in the mbar pressure range.^{4–6} Simultaneous accumulation of X-ray photoelectron spectra (XPS)^{5,6} shows that the oscillations are controlled by the reversible bulk oxidation of Ni to NiO. During the high-active half-periods nickel is in the metallic state, whereas during the low-active half-periods the catalyst surface is covered with a layer of NiO at least 3 nm thick.⁵ According to gas chromatography (GC) measurements the conversion of propane oscillates within a range from 23% to 1% indicating that the reactivity of metallic Ni is significantly higher than that of NiO.

In this paper we present the results of our further *operando* study of the self-sustained kinetic oscillations in the catalytic oxidation of hydrocarbons. Methane was chosen because according to the previous studies^{7–11} the similar regular oscillations have

been observed in the oxidation of methane over Ni under oxygen-deficient conditions within the temperature range between 650 and 900 °C. The period and the waveforms of the oscillations strongly depend on the reaction temperature, the CH₄:O₂ molar ratio, the catalyst type, and the detailed construction of the reactor used. It should be, however, noted that contrary to propane, the oscillations in the oxidation of methane occur only at atmospheric pressure. This makes it impossible, at least now, to apply XPS for characterization of the sample in the course of oscillations. To solve this problem *in situ* X-ray diffraction (XRD) was used in this study. In order to transfer the *in situ* study to *operando* one, mass spectra from reagents and products were measured together with XRD patterns.

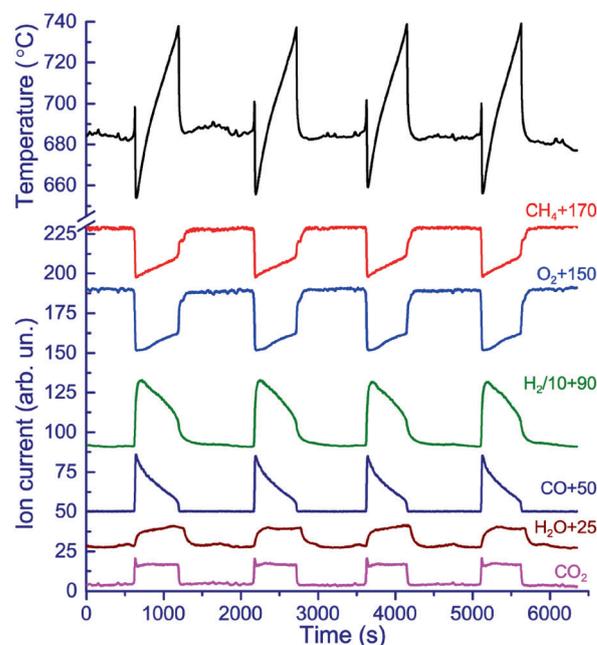


Fig. 1 Typical oscillations observed in the flow reactor at atmospheric pressure. The temperature of the flow reactor is 720 °C. The molar ratios CH₄:O₂:Ar are 2:1:17. The total flow is 50 sccm.

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In the first set of the experiments we performed the kinetic measurements. A flow quartz reactor described in detail elsewhere¹¹ was used in these experiments. The flows of methane, oxygen, and argon were regulated separately with mass-flow controllers SEC-Z500 (Horiba Ltd.). Rectangular pieces of 0.125 mm thick nickel foil 4 × 8 mm in size (purity 99.99%, Advent Research Materials Ltd.) were used as the catalysts. The catalyst temperature was monitored with a K-type Kapton-isolated thermocouple spot-welded directly to the foil. The products and reactants were analyzed using a quadrupole-type gas analyzer UGA-100 (Stanford Research Systems Inc.) connected to the reactor outlet through a stainless steel capillary of 0.175 mm inner diameter and 1 m length.

Typical oscillations observed during the oxidation of methane over Ni foil are presented in Fig. 1. The oscillations are relaxation type. The catalyst in a low-active state is activated occasionally with consumption of the reagents (CH₄ and O₂) and evolution of the reaction products: H₂, CO, and CO₂. Mass-spectrometric detection of H₂O, which is one of the reaction products, is complicated due to a high level of the residual pressure of water. The low-active and the high-active states are characterized by the methane conversion of 5% and 47%, respectively.

Such product distribution indicates that both partial and total oxidation of methane occur. Within a wide range of the molar ratio CH₄:O₂ from 12:1 to 2:1, the amount of burned-out methane is similar to that of oxygen consumed during the high-active half-periods, indicating that the partial oxidation of methane to CO and H₂ dominates. In contrast, during the low-active half-periods the ratio of the amount of burned-out methane and the amount of consumed oxygen depends on the molar ratio CH₄:O₂.¹¹ Thus, an increase in the oxygen content leads to a decrease in the selectivity toward CO. It has been also found that the period of oscillations can vary from approximately 200 to 4000 s by changing only the CH₄:O₂ molar ratio.

The oscillations of the products and reactants are accompanied by the regular variation of the catalyst temperature with peak-to-peak amplitude of more than 80 degrees (Fig. 1). Since the reactor is heated by electric furnace operated at the fixed power, these temperature oscillations cannot be a result of heating artefacts. Then, the release and removal of the heat in the course of chemical reactions occurring on the catalyst surface is the most likely reason of the temperature oscillations. An additional argument in favour of this explanation is the absence of a temperature variation in the low-active period of the oscillations. This phenomenon was discussed in detail elsewhere.¹¹ In short, we supposed that the sharp decrease in the catalyst temperature observed synchronously with the increasing CO signal is due to the endothermic reduction of nickel oxide: NiO + CH₄ → Ni + CO + 2H₂ ($\Delta H_{1000}^0 = +50.9 \text{ kcal mol}^{-1}$). The following monotonic increase in the catalyst temperature is due to the exothermic oxidation of methane over Ni: CH₄ + 2O₂ → CO₂ + 2H₂O ($\Delta H_{1000}^0 = -191 \text{ kcal mol}^{-1}$) and CH₄ + 0.5O₂ → CO + 2H₂ ($\Delta H_{1000}^0 = -5.2 \text{ kcal mol}^{-1}$).

In order to establish the changes in the catalyst state during the reaction-rate oscillations the *operando* XRD-MS study

was performed using the High Precision Diffractometry station at the synchrotron radiation facilities of the VEPP-3 storage ring (Siberian Synchrotron and Terahertz Radiation Center, Novosibirsk, Russia). The experiments were carried out on a high-precision X-ray diffractometer equipped with a collimation system, a high temperature reaction chamber, as well as with the same flow mass controllers and gas analyzer which were used in the kinetic experiments (Fig. 1). The reaction chamber, which was used as a flow reactor, was made from stainless steel and had a construction similar to a XRK-900 (Anton Paar GmbH). To prevent a contribution to the catalytic reaction from reactor walls, the inner part of the reaction chamber was coated by α -Al₂O₃ using a detonation spraying technique. The time-resolved XRD experiments were performed using a position sensitive parallax-free linear OD-3M detector.¹² The X-ray wavelength of 1.724 Å was set by a single reflection of the synchrotron radiation from a double Ge(111) single-crystal monochromator. The catalyst temperature was also measured by a K-type thermocouple.

In spite of the different constructions of the reactors used, the regular self-sustained oscillations were also observed in the XRD experiments. Under similar conditions the period of oscillations was approximately 170 s, which is long enough for a measurement of a series of diffraction patterns with an acceptable signal-to-noise ratio. The acquisition time of the XRD pattern in the 2θ range of 40–50° is approximately 10 s. Fig. 2 shows XRD patterns of the Ni foil measured during the self-sustained oscillations in the oxidation of methane. Only XRD reflections corresponding to metallic Ni and NiO oxide were observed. The intensity of these reflections oscillates simultaneously with the partial pressures of products and reactants, as well as with the catalyst temperature; intensity of the Ni and NiO reflections being changed in antiphase. The typical oscillations are presented in the inset in Fig. 2. One can see that the yields of CO, CO₂, and H₂ are maximal when the NiO signal is zero.

Fig. 3 shows the characteristic XRD patterns measured for the low-active and high active states of the catalyst. The high intensity of the NiO(111) and NiO(200) reflections is observed when the catalyst is in the low-active state. The transition to the high-active state is accompanied by a considerable enhancement of the Ni(111) reflection intensity and a complete disappearance of the nickel oxide patterns. It means that the self-sustained reaction-rate oscillations in the oxidation of methane over Ni originate from periodical oxidation and reduction of the catalyst. Taking into account the results of our previous study^{5,6} we can postulate that the relaxation-type self-sustained kinetic oscillations in the oxidation of methane and propane are due to the reversible bulk oxidation of Ni to NiO, the period of the oscillations being ranged from several seconds to several minutes for both systems. In spite of a great difference in pressures (atmospheric pressure for the methane oxidation or millibar pressure range for the propane oxidation), metallic Ni demonstrates a higher activity in both reactions than NiO, at least under oxygen-deficient conditions. Similar conclusions have been made in recent articles



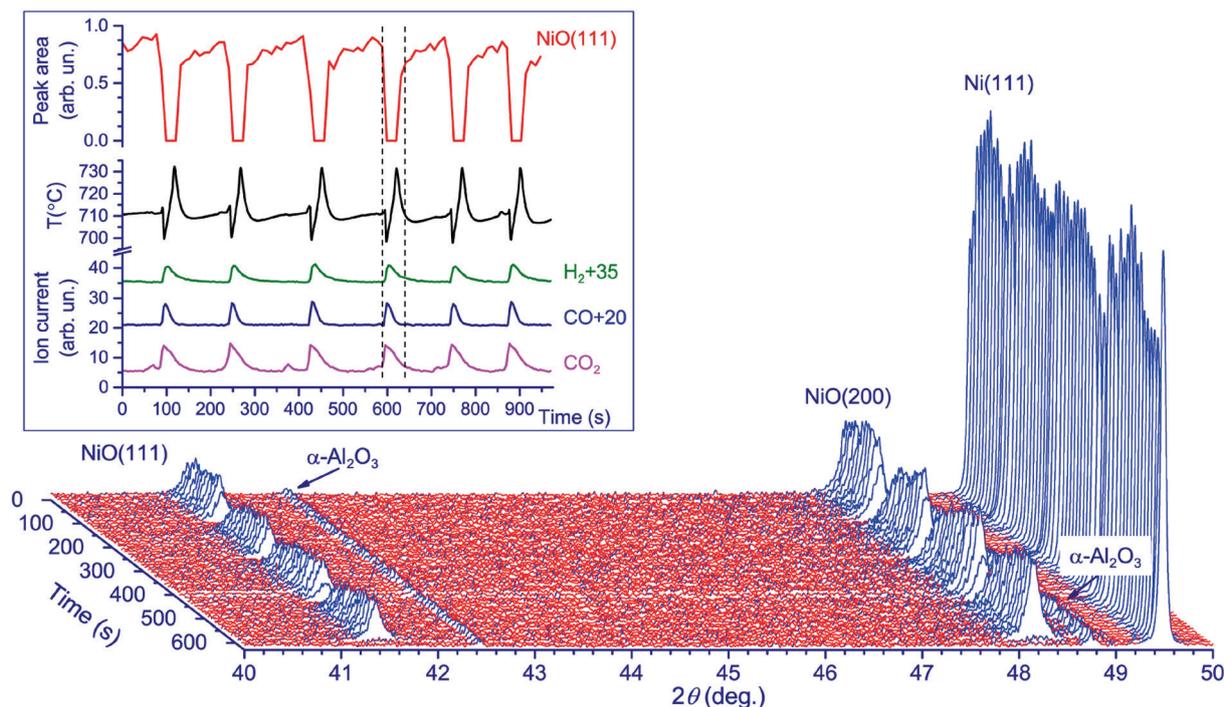


Fig. 2 XRD patterns obtained during the *operando* measurements. Corresponding oscillations of MS signals, catalyst temperature, and integral intensity of the NiO(111) peak are presented in the inset. The molar ratios CH₄:O₂:Ar are 4:1:15. The total flow is 100 sccm. The reflections of α -Al₂O₃ are due to alumina deposited on the Ni foil as a reference.

devoted to the study of self-oscillations in the methane oxidation over Pd. For example, Bychkov *et al.*,¹³ who studied the oxidation of methane over supported Pd/Al₂O₃ catalysts using *in situ* thermogravimetry and mass spectrometry (MS), showed that metallic Pd exhibits the highest activity in the total oxidation. Oxidation of the metal surface decreases sharply the catalytic activity.

Analogous results were also obtained by Stötzel *et al.*¹⁴ who also studied the self-sustained oscillations in the same catalytic system using the *operando* X-ray absorption spectroscopy (XAS) and MS techniques. They observed the formation of H₂ and the consumption of O₂ from gas phase when Pd

was mainly in the metallic state, whereas the intensity of H₂ signal was negligible when Pd was oxidized to PdO.

These findings contradict several reports on catalytic oxidation chemistry. Thus, it has been concluded that late transition metal oxides such as RuO₂, PdO, and IrO₂ are more active in the catalytic oxidation of hydrocarbons than the corresponding metals.¹⁵ For example, Martin *et al.*¹⁶ studied the oxidation of methane on Pd(100) by XPS in the mbar pressure range and showed that a high activity was achieved when a two-layer oriented film of PdO(101) was formed on the palladium surface. Using DFT calculations, they showed that the presence of oxygen atoms directly below coordinatively unsaturated (cus) palladium atoms in the two-layer oxide film was crucial for the efficient dissociation of methane.

From this point of view we can suppose that the reasons of lower activity of nickel oxide are due to the absence of coordinatively unsaturated nickel atoms on the upper layer of NiO. However, the surface structure of nickel oxide under reaction conditions is not understood yet, and we cannot make any definitive conclusion about the main reasons for a lower reactivity of NiO in comparison with metallic Ni. A possible reason for this could be a lack of cus-sites at the predominant facets of formed NiO under reaction conditions. Differences in the energetics of extracting lattice oxygen from the oxides could also be important.

These contradictions require new opportunities to study the mechanism of these catalytic reactions. An *operando* approach, which combines the catalyst characterization

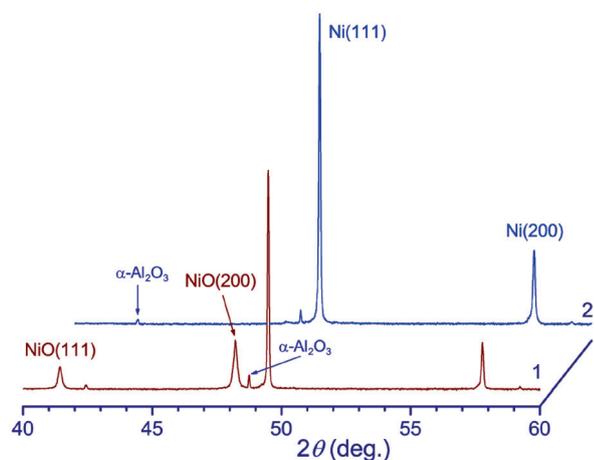


Fig. 3 XRD patterns obtained during the low-active half-period (1) and the high-active half-period (2).



with modern techniques such as XPS, XAS, or XRD and the measurement of catalytic activity with MS or GC,¹⁷ together with the self-oscillation mode of the reactions allow one to establish the catalyst state during both low-active and high-active half-periods of oscillations, to understand the reasons causing the transition between these states, and, finally, to elucidate the mechanism of the reaction under study.

Summarizing our results, we can maintain that the Ni-based catalysts can undergo some irreversible modification under reaction conditions, which influences their catalytic performance and initiates the oscillatory behaviour. This modification is due to a change in the chemistry or morphology⁶ of near-surface layers of the catalyst. The self-sustained reaction-rate oscillations occur because of the periodical transition between metallic Ni and NiO, which may proceed through some transient states, such as a solid solution of oxygen in metallic nickel or highly defective nickel oxide.⁶ The rate of oxidation of methane¹¹ and propane^{5,6} is at least 10–20 times higher over metallic Ni than that over nickel oxide. On the metallic surface, the oxidation proceeds through the Langmuir–Hinshelwood mechanism, while over the oxidized surface, the reaction proceeds *via* the Mars–van Krevelen redox sequence. In the first case, the molecules of reactants adsorb and dissociate to form the adsorbed C, H, and O atoms which can react to form products or to modify the catalyst. For instance, accumulation of carbonaceous deposits¹¹ or dissolution of C and O atoms in the sub-surface layers of Ni may cause a decrease in the activity and selectivity toward CO and H₂, as shown in Fig. 1. After an increase in the concentration of dissolved oxygen to some limit, the spontaneous transition to the NiO structure may occur. Again, adsorption of methane over NiO generates oxygen vacancies, which can accumulate during the low-conversion period. As shown by Groppi *et al.*,¹⁸ a sub-stoichiometric oxide or highly O-defective PdO are highly active compounds in the oxidation of methane. Indeed, a vacancy is required to activate the first, rate-determining step: H-abstraction from CH₄.¹⁹ Accordingly, after an increase in the amount of the oxygen vacancies in the NiO structure to some limit, this high-defect oxide becomes unstable and transforms to metallic Ni. These processes can repeat regularly in time to initiate the self-sustained reaction-rate oscillations in the oxidation of methane over Ni.

Conclusions

Finally, we can conclude that the investigation of the self-sustained reaction-rate oscillations by *operando* techniques is a powerful tool for a mechanistic study. It allowed us to show that the main reason for the appearance of the reaction-rate oscillations in the oxidation of methane is the reversible bulk oxidation of Ni to NiO; metallic Ni in the catalytic oxidation of methane is more active than NiO.

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