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Thermography study of propane oxidation to synthesis-gas over nickel

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Abstract

Propane oxidation to the synthesis-gas over a metallic nickel ribbon in a self-oscillation mode has been studied by mass-spectrometry and in situ thermography. The combined application of these methods has shown that the oscillations of the reaction rate are accompanied with periodic changes of the catalyst temperature, with the half-periods of high reaction rate being correspondent to the sufficient rise of the catalyst temperature. It has been concluded that this additional heating of the surface is due to heat evolution during this exothermic reaction. The use of thermography made it possible to detect also the formation of ‘hot spots’ on the nickel surface during the half-period of high activity. It has been, however, shown that the ‘hot spots’ are not responsible for the formation of the oscillations. Possible reasons for the ‘hot spot’ formation in this system are discussed.

Keywords: Mass-spectrometry; Thermography; Nickel; Propane oxidation

1. Introduction

One of the general problems in heterogeneous catalysis is a measurement of real temperature of an active component of an operating catalyst. This problem is most important for the supported catalysts, which represent small (<100 nm) metal particles supported on a dielectric ceramic (Al_2O_3, SiO_2) with low thermoconductivity. Consequently, exothermic catalytic reactions (oxidation, hydrogenation, etc.) can result in overheating of the metallic particles as compared to the support. In an extreme situation, when the heat exchange between an active component and a support is determined by a thermoradiation, the overheating can exceed a 100° [1]. This effect can be of a great importance also for the monometallic catalysts provided that the reaction conditions are severe enough to modify the subsurface catalyst layers by its components, in extreme cases to transform the metallic phase to the oxide ones. Again, the temperature of a catalyst surface (catalytic reaction proceeds on the surface) will be different from the bulk temperature measured using a thermocouple. And at last, the problem of local overheating is well-known for catalyst beds in commercial reactors (the problem of ‘hot spots’).

The experimental observation of the overheating of a catalyst active component is of great significance for the catalytic theory and practice, since it means that the catalyst temperature measured by standard methods (for example, using a thermocouple) can be quite different from the real temperature of a catalytic process. To observe a real temperature of a catalyst surface, we propose to use thermography, which allows the measurement not only of average temperature of a surface, but also of temperature distribution on it [2–4]. The latter is of importance to study the ‘hot spot’ problem. Obviously, the planned experiments should be carried out in situ, i.e. in the case of an operating catalyst, as only under influence of a catalytic reaction we can expect evolving the reaction heat and overheating of the reaction zones on a catalyst surface.

In this paper, we report a first application of in situ thermography to study a catalytic reaction—partial oxidation of propane to the synthesis-gas over metallic nickel. This system was chosen on the basis of our recent experimental data,

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which showed that under specific conditions the oxidation of propane over nickel can occur in a self-oscillatory mode [5,6]. The oscillations of the reaction rate were found to be accompanied with significant changes in the catalyst temperature. This result has allowed us to hope that thermography can measure a variation of the surface temperature during the self-oscillation of the reaction rate and, may be, even temperature distribution on the catalyst surface in the case of its inhomogeneity.

Note, the formation of ‘hot spots’ on the catalyst surface is considered in literature as a possible mechanism of the formation of thermokinetic oscillations. Other mechanisms, which are discussed as possible reasons for the non-isothermal oscillations [7–9], are a periodic oxidation/reduction of the catalyst surface [10] and a formation/destruction of surface carbides, etc. The elucidation of the relevance of these mechanisms in the case of the oscillations during the propane oxidation over nickel was also the aim of this study.

2. Experimental

To apply the thermography for the investigation of heterogeneous catalytic reactions, a catalytic flow reactor of a special construction was designed and built in our laboratory. An external view of the reactor for in situ thermography and its simplified scheme are shown in Fig. 1. The construction of the reactor allows:

(i) evacuation of the reactor with the aim of removal of background gases;
(ii) introduction of gases inside the reactor to make a reaction mixture with various content;
(iii) resistive heating of the sample;
(iv) recording the thermography images of a sample via sapphire window.

The application of sapphire as a material for the optical window makes it possible to measure the surface temperature both in infrared (25–350 °C) and in visible (>500–1000 °C)

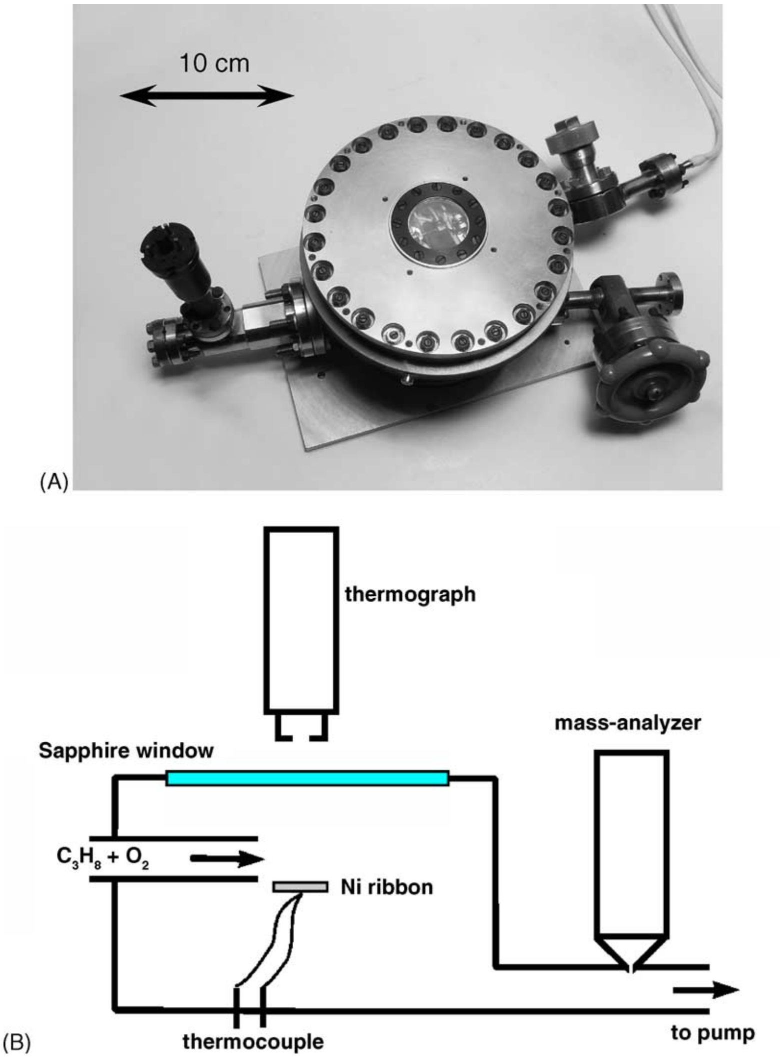

Fig. 1. External view of a designed reactor for in situ thermography (a) and simplified scheme of the experimental set-up (b).

ranges. The temperature resolution of our thermograph was 0.05 °C, and the surface resolution in the visible range was 2 μm. The catalytic reactor was attached through the pinhole leak ($d = 0.2$ mm) to a UHV set-up equipped by a quadrupole mass-analyzer for detection of the gas-phase composition.

In this study, a nickel polycrystalline foil was used as a model catalyst for the propane oxidation to the synthesis-gas. The foil was resistively heated with the direct current to the temperature of 650 °C. The power supply unit could operate both as a voltage source and as a current source. It was experimentally tested that the stabilization mode of the power supply unit did not affect the behaviour of the reaction system. The nickel foil in the form of a ribbon was installed perpendicular to the reagent flow; in Fig. 1, it is shown as a cross-section. The heated catalyst was dosed to propane and oxygen with the flow rate of 1 Ncm^3/s. The ratio of propane and oxygen in the feed was $C_3H_8/O_2 = 9/1$. The pressure in the reactor during the experiments was 1 Torr.

The thermograph was calibrated in argon with a chromel–alumel thermocouple, which was spot-welded to the backside of the catalyst ribbon. By illuminating the catalyst with several glow lamps, we could also obtain images of the catalyst surface in reflected light. This gave us a possibility to detect the morphology of the catalyst surface.

3. Results and discussions

A time-variation of partial pressures of a number of the reagents and reaction products of the propane oxidation over a nickel catalyst is shown in Fig. 2. One can see that the reaction periodically passes through the periods of high activity ($t = 30$–80 and 220–270 s), when the formation rate for all products is maximal. These periods alternate the periods of low activity ($t = 0$–30 and 80–220 s). The half-periods of high catalytic activity are characterized by oxygen uptake. This behaviour indicates that under these experimental conditions and in the designed reactor, the oxidation of propane over nickel still can operate in the oscillation mode. It was not so evident, since the procedure of this experiment was quite different from that used in our previous work [5]. Earlier [5], the catalyst was installed inside a quartz reactor heated with an oven wound outside the reactor. As a consequence, the sample temperature was maintained due to the heat transfer through the gas phase. The construction of the thermography reactor, which was made from stainless steel (Fig. 1), required the application of the resistive heating of the sample, whereas the gas mixture was passed through the reactor at ambient temperature (see Section 2).

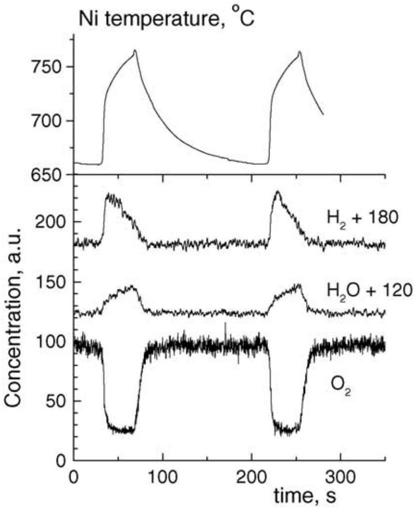

Fig. 2. Simultaneously detected oscillations of catalyst temperature and concentrations of the reaction products and O_2 at the reactor outlet.

Fig. 2 shows also the variation of the surface temperature with time. One can see that the oscillations of the reaction rate are accompanied with the periodic changes of the catalyst temperature, and the half-periods of high activity correspond to the sufficient rise of the catalyst temperature. It should be noted that the variation of temperature in the quartz reactor [5] had the opposite character. There, the half-periods of high activity were accompanied with a sufficient decrease in the catalyst temperature. Thus, the oscillations of the rate of propane oxidation over nickel do not depend on the direction of the changes in the catalyst temperature. This result allows us to suppose that the oscillation mechanism in this system is not described in the framework of thermokinetic oscillations. In the model of thermokinetic oscillations, namely the rise of the catalyst temperature at the specific time of a reaction results in a transition of the reacting system into the region limited by diffusion [8].

Although we do not have an evident explanation of the contradictory temperature behaviours in these two experiments now, the application of thermography indicates unambiguously that the catalyst surface indeed is heated when the reaction rate of the propane oxidation is high. As a consequence, we can suggest that namely the heat, which evolves during surface chemical reaction steps (both partial and total oxidation of propane are the exothermic reactions), causes the increase in the surface temperature. It is obvious that to provide such considerable heating of the surface (up to 100 °C) during the reaction, dissipation of the heat inside the nickel bulk should be limited. A possible candidate, which could provide this effect, is a phase of nickel oxide, the formation of which has been concluded by us recently [6] on the basis of the XPS data.

Another possible reason for the switching of the propane oxidation into the oscillatory mode – the formation of ‘hot spots’ – can be checked by thermography. In this model, ‘hot spots’ reflect most active local elements (patches) of the surface, the temperature of which can be sufficiently higher than the temperature of the rest of the surface. Then, due to the heat generated by the reaction at these elements, the temperature of the whole surface can be increased and the reaction can expand onto the whole surface. In other systems [11], these elements migrated over surface.

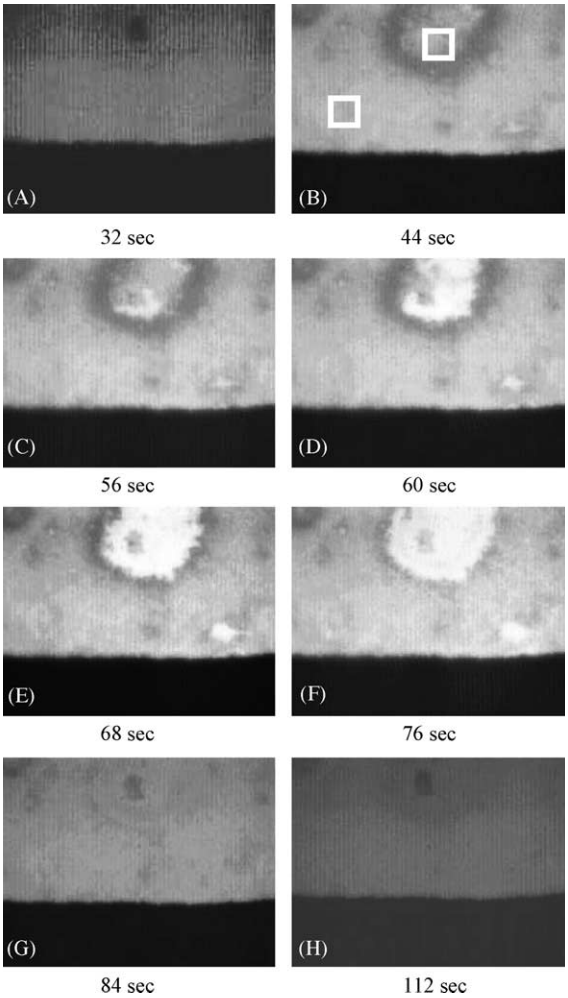

Fig. 3. Sequence of thermography images from the nickel foil measured during oscillatory oxidation of propane. The frame size is 500 μm × 750 μm.

Fig. 3 shows a set of thermography images of the same part of the nickel surface during the oscillatory oxidation of propane. The upper part of the images (about two-thirds) corresponds to the nickel surface, the lower part (one-third)—to the gas phase space. Time marked below each image corresponds directly to the points on the kinetic curves of Fig. 2. One can see that during the half-periods of low activity (before 44 s and after 84 s), the temperature of the catalyst surface is low (dark images) and rather uniform. Transition to the half-periods of high activity heats the surface (images become brighter and brighter), and different elements of the surface are characterised by different temperatures. To quantify this effect, we measured average temperature on two chosen patches, which marked in Fig. 3B as squares. The choice of the elements was based on the visual effects in the sequence of the thermography images: the upper square (1) increases its temperature to higher values than the square, which is located in the low/left part of the surface (2).

Fig. 4 shows the evolution of the averaged temperature of these surface elements with time. In full agreement with the visual effects, these surface elements have close temperatures during the half-period of low activity (Fig. 4). The similarity in temperatures of both squares remains during the period of time 30–55 s, when the surface heats sharply from 660 to ∼750 °C. However, then the temperature behaviour of these surface elements starts to differ. If the temperature of the element (2) is going to a plateau at 750 °C, the element (1) continues its heating up to the temperature of 765 °C. This result indicates that the overheated catalyst surface at the upper side of Fig. 3 has the temperature about 15 °C higher than the temperature of the other parts of the surface. The overheated part of the surface also exhibits a steep gradient of temperature at its boundary. Therefore, this region can be considered as a ‘hot spot’. It should be also noted that cooling of the nickel surface during transition of the reaction to the low-active half-period starts only at that moment when the temperature of the ‘hot spot’ is equalised with the temperature of the rest surface (Fig. 4).

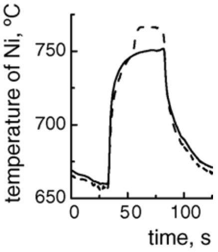

Fig. 4. Evolution of the temperature of two surface elements (see the square marks in Fig. 3B with time measured during an active half-period of the propane oxidation over nickel.

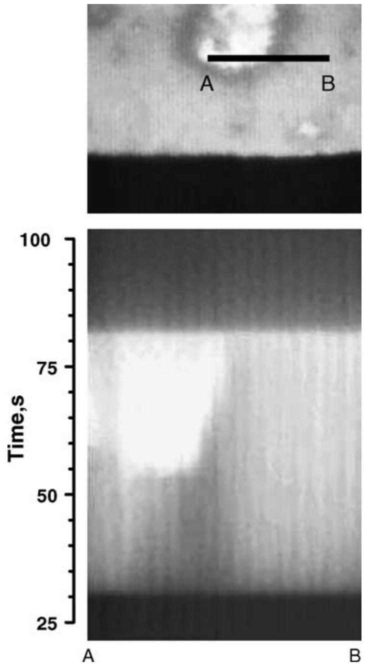

Fig. 5. Thermography image from the nickel surface (a) and evolution of the temperature of the segment AB (see the linear mark in (a)) with time (b) measured during oscillatory oxidation of propane. The frame size is 500 μm × 750 μm.

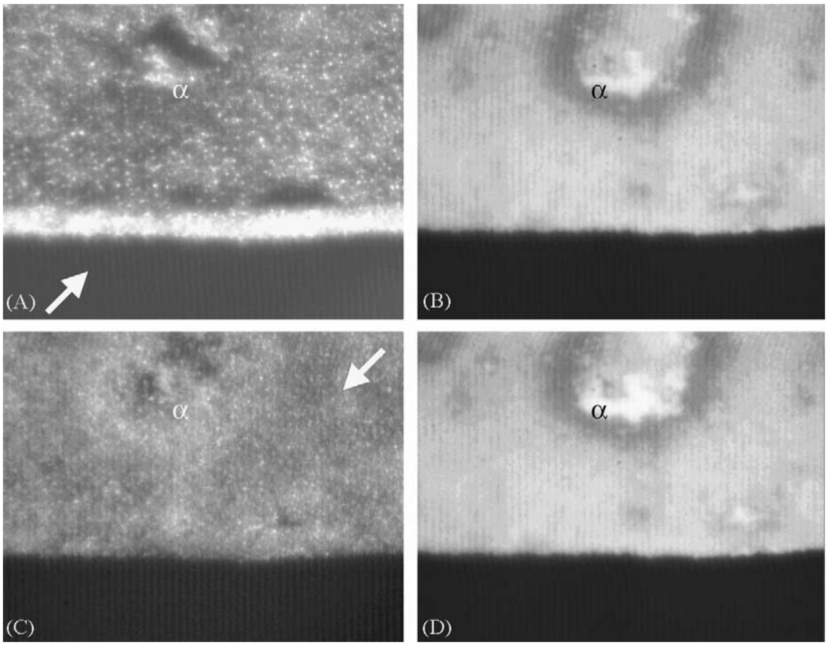

Fig. 6. Images of the nickel surface recorded in the reflected (A and C) light and thermography images (B and D) from the same part of the nickel surface measured during oscillatory oxidation of propane. The white arrows show the direction of incident light. The frame size is 500 μm × 750 μm.

An additional capability of the thermography is demonstrated in Fig. 5, which shows the variation of temperature of the linear segment AB with time. The chosen segment is spread away the border of the 'hot spot' (Fig. 5a) that could help us to observe a possible movement of the hot zone on the surface. In full agreement with the data of Fig. 4, the 'hot spot' appears at about 55 s that is considerably later than the beginning of the active half-period at 30 s. Thus, the reaction is switched into the active half-period even before the formation of 'hot spots'. Other interesting observation, which can be seen from Fig. 5b, is the fact that the 'hot spot' does not spread over the whole catalyst surface. Both these results unambiguously show that the switching of the reaction between the half-periods of low and high activity is not caused by the formation of the 'hot spots' and their propagation on the surface.

To evaluate the possible reasons for the appearance of 'hot spots', we measured the images of the catalyst surface under its illumination by reflected light (see Section 2). An analysis of such images allows a reconstruction of the surface relief. Fig. 6A and C shows the images of the catalyst surface taken with the illumination from different directions shown with the arrows. The thermography images of the same part of the surface measured at different moments of the kinetic curve shown in Fig. 6B and D indicate the presence of the 'hot spot' in the analysed patch of the surface.

It is seen that the bright regions in Fig. 6A corresponds to the dark regions in Fig. 6C. It means that these regions have different reflectance, most probably, due to different slopes with respect to the incident light. Similar analysis, performed also for the images obtained upon the illumination under other angles of the incident light, shows that the bright region denoted with α in Fig. 6A corresponds to a protrusion on the catalyst surface, but not to a cavity. Using surface resolution of our technique, we have estimated the height of this protrusion, which does not exceed 20 μm. A comparison of the surface images measured in the reflected and the emitted (thermography) light indicates that the 'hot spot' appears at the protrusions (Fig. 6B) and then occupies a restricted region of the catalyst surface (Fig. 6D). One can see also that the 'hot spot' does not migrate over the surface.

It is noteworthy that this restricted region corresponds to the place on the catalyst surface, underneath of which the thermocouple was spot-welded. It is evident that with such method of the thermocouple fastening, this place can have different properties than the rest of the surface. In other words, the use of thermocouples can lead to the appearance of side effects, which should be taken into account during a preparation and carrying out of other catalytic experiments in order to avoid a misinterpretation.

4. Summary

The combined application of mass-spectrometry and thermography allowed us to show that the oscillations of the rate of propane oxidation to the synthesis-gas over metallic nickel are accompanied with the periodic changes of the catalyst temperature. The half-periods of high activity correspond to the sufficient rise (up to 100°) of the catalyst temperature, most probably, due to heat evolution during this exothermic reaction. The transition to the half-period with the low reaction rate cools the sample.

The thermography demonstrates also the formation of ‘hot spots’ on the nickel surface during the oxidation of propane in the oscillatory mode. It has been, however, shown that the ‘hot spots’ are not the reason for the formation of the oscillations. As a consequence, the mechanism of the formation of the oscillations cannot be described in the frames of the thermokinetic oscillations.

Acknowledgements

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