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Oscillations during catalytic oxidation of propane over a nickel wire

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Catalytic oxidation of propane with oxygen over a nickel wire at the temperature range 650–750 °C and the reagent pressure *ca.* 1 Torr occurs in a self-oscillating mode. Periodic changes of the reagent concentration are found to be accompanied by significant synchronous changes of the catalyst temperature.

KEY WORDS: self-sustained oscillation; nickel; oxidation; propane

1. Introduction

Oxidation of propane with oxygen attracts a considerable attention due to its practical and theoretical importance. More than a hundred papers devoted to this reaction were published the last few years. Various catalysts, such as vanadia, molybdena, zeolites, *etc.* have been studied. We found that metal Ni can stimulate self-sustained oscillations of the reaction rate.

In the last few decades, numerous heterogeneous self-oscillating reactions have been reported in literature (see, *e.g.*, reviews in [1–3]). Mostly, the oscillations were observed for the heterogeneous oxidation of CO, hydrogen and olefins. As to the oscillating modes at oxidation of alkanes, these reactions are considered to be mostly homogeneous gas-phase reactions such as cool flames. Only few examples of catalytic oscillating oxidation of light alkanes have been published to date [4,5].

Despite a great number of papers on oscillating reactions, there is still a lack in deep understanding their mechanisms. The most developed mechanisms are suggested for the oscillatory oxidation of H_2 and CO. In more complicated cases of oxidation of hydrocarbons, the mechanisms of the oscillations are less clear. In this paper, we report on the first detection of self-sustained oscillations at heterogeneous catalytic oxidation of propane. An attempt is made to reveal the phenomenology of the oscillatory mode of the catalytic propane oxidation and to understand the role of both heterogeneous and homogeneous processes in the mechanism of the reaction. Although a mechanism of such complicated process as an oscillating reaction cannot be proved within the limits of one paper, we hope that this work will stimulate the interest and further investigation of the reaction.

2. Experimental

The experimental setup is schematically shown in figure 1. The reactor was made of fused quartz. The catalyst was a nickel wire 1 m long with a diameter of 0.1 mm folded in the reactor without self-intersection. To avoid the intersection, most of the wire ($\sim$70%) was coiled around two conjunct quartz bobbins. The other 30% were the electrical leads. The bobbins are not shown in figure 1 for simplicity. The catalyst was used simultaneously as a resistance thermometer calibrated in a flow of argon at the same pressure and flow rate as in the reaction. The gas temperature near the Ni coil (see figure 1) was detected independently with a thermocouple. To prevent heterogeneous reactions on the thermocouple surface, the thermocouple has been covered with quartz.

The reaction products were detected using a quadrupole mass-analyzer MC7303 (USSR) with a sampling time less than 0.1 ms [6].

The reaction was carried out at pressure 1 Torr at temperatures from 600 to 850 °C. A propane/oxygen mixture was fed into the reactor with the flow rate 1 Ncm^3/s. The oxygen concentration in the mixture was 5 vol%.

Three sets of experiments were made.

In the first set, the catalyst was heated only with an electric oven from outside of the reactor due to the heat transfer through the gas phase. In this case, the electric current of 8 mA was used to measure the resistance of the nickel wire. As it was checked experimentally, such low current itself does not result in any detectable rise of the catalyst temperature.

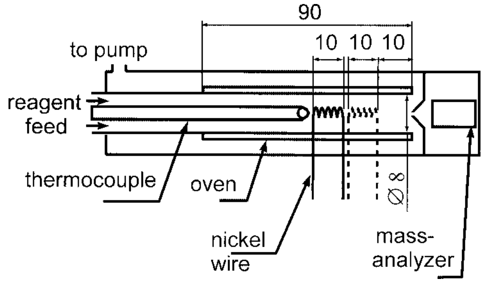

Figure 1. Simplified scheme of the experimental setup. The dashed line shows the position of the second wire used in the third set of experiments. The distance between the wires was 2 mm. The position of the first wire was the same in all experiments. (All numbers are in mm.)

In the second set of experiments, the catalyst was heated additionally with passing the direct electric current of 500 mA through the wire. This allowed us to vary the catalyst temperature independently of that of the gas phase.

In the third set of experiments, we used two separate nickel wires of the same length (figure 1). Their resistances were monitored simultaneously. The electric current used was 8 mA as in the first set of the experiments. No additional heating of the catalysts was applied in this set. In all the experiments, the concentrations of oxygen, hydrogen and water were monitored simultaneously during the propane oxidation with the use of the mass-analyzer.

3. Results and discussion

In the temperature range 600–800 °C, both partial and complete oxidation of propane over Ni is known to occur. We observed the occurrence of both these reactions *via* detecting the consumption of O_2 and the evolution of H_2O and H_2. Unfortunately, the mass-spectrometric detection of the evolution of CO, CO_2 as well as propene was not possible against the background of the propane excess. The mass-spectra of these substances were masked by the fragmentation pattern of the propane mass-spectrum. Observing the concentrations of O_2, H_2O and H_2 at the reactor outlet unexpectedly revealed that in a particular range of the gas-phase temperature, the reaction starts to operate in a self-sustained oscillatory mode. When using shorter wires without the supporting bobbins (sometimes it led to the self-intersections of the nickel wire), all the found peculiarities of the reaction remained unchanged. The oscillations of the gas phase and of the temperature were sufficiently the same, however being measured with larger noises. The controlling experiments were also carried out both with and without the bobbins, and it also made no difference in the results.

3.1. The first set of experiments

Figure 2(A) shows a typical oscillation pattern observed for the O_2, H_2O and H_2 concentrations when providing the experiment through heating only the gas phase. Clear self-sustained oscillations of a relaxation type [1] were detected only in the presence of nickel at the gas-phase temperatures from 650 to 750 °C. The controlling experiments carried out under the same conditions in the catalyst absence showed that the uncatalyzed reaction exhibits only a stationary behavior. The kinetic curves recorded with the void reactor are shown in figure 2(B).

It was also found that a freshly installed catalyst does not initiate the oscillations. The oscillations appear only after several hours of the catalyst operation in the reaction. Evidently, the induction period for the oscillations cannot be explained in terms of a pure homogeneous gas-phase mechanism of the reaction. Under the reaction conditions, the gaseous reagents are renewed every 6 ms, so the presence of the hour-scaled effect would mean the existence of some slow heterogeneous reactions. We suppose that the induction period mentioned above appears due to the formation of an active structure on the catalyst surface. Presumably, nickel oxide, which covers the fresh nickel wire, is being reduced and the surface morphology of the nickel wire is being reconstructed under exposure to the reaction mixture. According to the XDS data, the above catalyst treatment leads also to an enlargement of the nickel crystallites in the metal bulk.

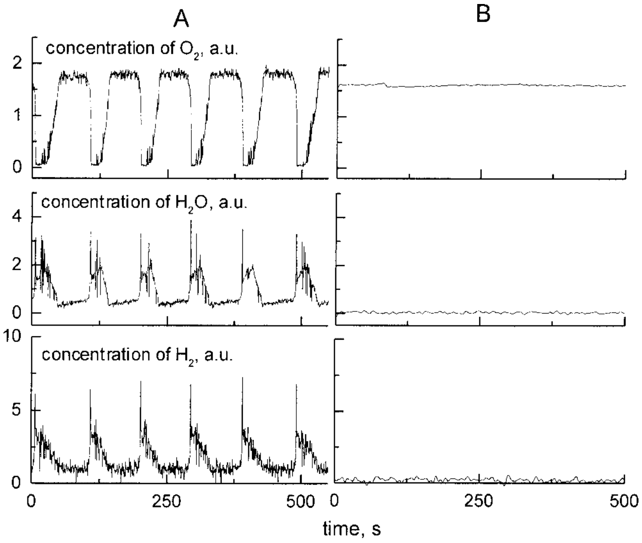

Figure 2. Oscillations of the concentrations of O_2, H_2O and H_2 detected simultaneously at the reactor outlet in the presence of the Ni wire (A) and in the void reactor (B). The temperature of the gas phase is 750 °C.

It was also found that if the sample which has initiated the oscillations is cooled down in the flow of the reagents, one can leave the sample on air for months and then it “switches on” the oscillations immediately after exposing to the reaction mixture, with no induction period. The procedure of cooling the catalyst in the reagent flow is similar to that used to passivate the Ni catalyst designed for the filament carbon formation from methane [7]. It has been shown that the procedure prevents the formation of oxides on the Ni surface.

We suppose that the above “memory” effect and the presence of the long induction period for the oscillations indicate clearly the participation of some heterogeneous reactions in establishing the oscillations. One may expect that the periodic formation of NiO as well as the dissolution of carbon, hydrogen and oxygen [8] in nickel are essential in these processes. As shown recently by Schlögl *et al.* [9], similar processes can generate kinetic oscillations during the methanol oxidation over a Cu metal catalyst.

As shown in figure 3, in our case the oscillations of the oxygen concentration are accompanied by periodic changes of the catalyst temperature. Although no additional heating was applied in this set of experiments, the detected catalyst temperature was 50 °C over that of the gas phase. This additional heating of the wire should be attributed to releasing the heat of the catalyzed reaction. Unexpectedly, the detected consumption of oxygen appeared to be coinciding with a decrease in the catalyst temperature while the detected temperature of the gas phase remained constant.

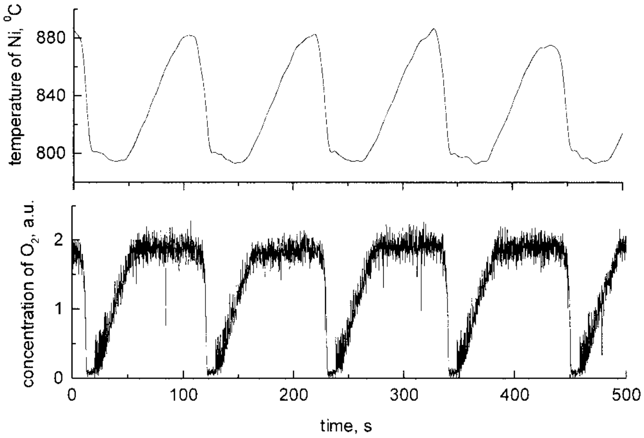

Figure 3. Simultaneously detected oscillations of the catalyst temperature and of the O_2 concentration at the reactor outlet. The temperature of the gas phase is 750 °C.

Note that the resistively measured increase in the catalyst temperature cannot be explained with the decrease in the metal-wire cross-section due to the formation of an oxide layer. Against such an assumption testifies the magnitude of the temperature oscillations. Indeed, the detected rise in the wire resistance, as well as the detected temperature rise, reach 10%. In case of the constant temperature, this change could be caused by diminishing of the radius of the metal wire by $\sqrt{10}/2\%$. With the initial wire diameter of 100 μm, the thickness of the non-conducting oxide layer has to be no less than 1 μm. The formation of the so thick oxide layer seems to be hardly possible at the experimental time scale. The period of the oscillations is about 100 s. With the oxygen flow rate 0.05 Ncm^3/s, about 10^{20} molecules of oxygen come into the reactor during this time. Even if all oxygen is consumed for the NiO formation, this amount of oxygen will be enough for the formation of only 1–2 monolayers of the oxide. Therefore, the detected changes in the resistance have to be of thermal nature.

At present, the mechanism of the catalyst temperature decrease, which coincides with the enhanced oxygen consumption, is not clear. Possibly, the periods of the oxygen consumption from the gas phase and the periods of its exothermal reactions on the surface do not coincide in time.

3.2. The second set of experiments

In this set of experiments, the temperature of the nickel wire was artificially raised by its direct resistive heating. Passing the direct electric current up to 500 mA through the wire permitted us to maintain the catalyst temperature oscillating in the same range, from 800 to 880 °C, as in the experiments above (figure 3), while the temperature of the gas phase could be diminished sufficiently. Figure 4 shows the oscillation of the reagent concentrations detected while the wire was heated through the gas phase (A) and the oscillation with the additional resistive heating of the wire (B). As shown in figure 4, if the catalyst temperature is kept high enough, the oscillations still appear at the gas temperature as low as 400 °C. Without the additional heating, the oscillations exist only at the gas temperatures over 650 °C. In both cases, the consumption of oxygen has the shape of time pulses. However, the character of the oscillations differs sufficiently in these two cases. The duration of the oxygen consumption pulses is much shorter at the lower temperatures of the gas phase than at the higher temperatures. The pulse shape differs sufficiently in these cases as well. At the lower gas temperatures, the leading edge of the oxygen consumption pulse is longer than the trailing one (see the cut in figure 4). In contrast, at the higher temperature of the gas phase, the leading edge is much shorter than the trailing one. The apparent differences in the oscillation modes registered at different temperatures of the gas phase seem to demonstrate a sufficient participation of some homogeneous reactions.

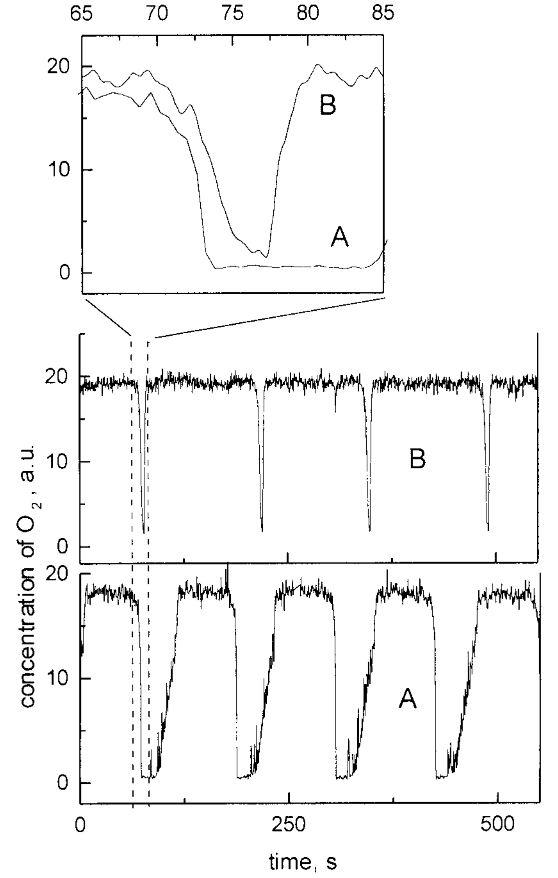

Figure 4. Different oscillatory patterns registered at different temperatures of the gas phase: (A) 750 and (B) 400 °C. In both cases, the catalyst temperature was maintained oscillating in the range 800–880 °C (figure 3).

3.3. The third set of experiments

To reveal some features of the mechanism of synchronization of local events on the catalyst surface or over it, which is responsible for the formation of macroscopic oscillations, we used two separate nickel wires located in the reactor without mutual electric contact. Simultaneous detecting the resistances of both wires showed that the temperature oscillations on the wires were in-phase, without a delay (figure 5).

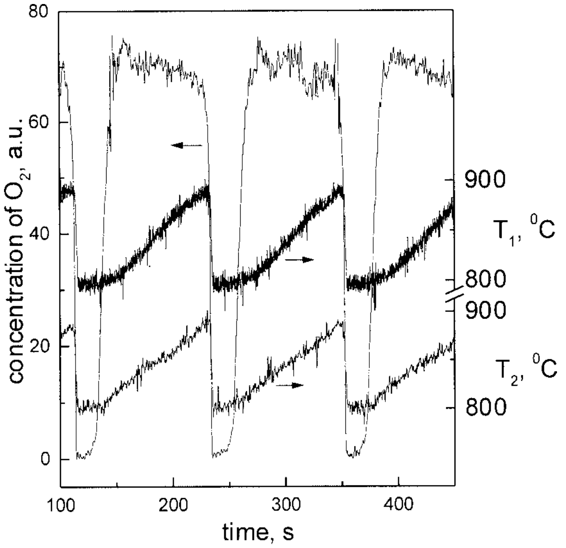

Figure 5. Synchronous oscillations of the temperatures T_1 and T_2 of two separate Ni wires and of the O_2 concentration in the third set of experiments. The temperature of the gas phase is 750 °C.

An analogous method was used by Tsai *et al.* [10] in the investigation of the CO oxidation on a Pt wire loop. They cut their loop into two halves and found that the oscillations of the CO oxidation rate on these two parts continued to have the same period but changed their shape. Unlike those results, the oscillation patterns in figure 5 remain sufficiently the same. We believe that our data evidence the complete synchronization of the catalyzed reaction on both wires through the gas phase.

Unfortunately, the resistance measurement only allows the detection of an averaged temperature of the long catalyst. More detailed information on the possible nonuniformity of the temperature along the wire is not available yet. Such nonuniformity was shown by Luss [11] to cause the oscillations in the gas phase. However, our experiments with two wires seem to indicate a fair uniformity of the catalyst surface provided by a strong coupling *via* the gas phase.

The above experiments evidence the necessity to explain the mechanism of the catalytic propane oxidation on metal Ni in terms of heterogeneous–homogeneous reactions. Note that usually the heterogeneous–homogeneous catalytic reactions are considered as involving free radicals as the reaction intermediates. Here we use the term “heterogeneous–homogeneous” in a general sense in order to mention an interference of surface reactions with reactions in the gas phase. Now, we are not able to claim the participation of free gas-phase radicals in the reaction under study. However, their possible role is a subject for a future study.

A very important problem seems to be the large discrepancies in the recorded temperatures of the catalyst and the reaction gas medium. Usually, to detect the temperature of a catalyst, thermocouples are used. To prevent heat-releasing or heat-consuming reactions on the thermocouple surface, the thermocouples are usually covered with an inert material. Evidently, when the catalyst consists of a highly dispersed metal loaded onto a chemically inert support, the procedure of the correct measurements of the temperature of the catalyst active phase becomes very difficult. The above-presented results indicate that the discrepancy between the actual temperature of the catalyst and the temperature recorded with an external thermocouple situated nearby the catalyst can be about 100 °C. It is clear that despite the simplicity and convenience of thermocouple units for the temperature measurements, their use in heterogeneous catalysis should be thoroughly revised when we need to know the real temperature of the catalyst active phase (see also [12]).

4. Conclusions

Catalytic oxidation of propane over a Ni wire at the temperature range 650–750 °C is shown to occur in a self-oscillating mode. The oscillations are accompanied with the significant oscillations of the catalyst temperature. A mechanistic scheme of the propane oxidation reaction has to include most probably both heterogeneous and homogeneous steps. Measuring the actual temperature of a catalyst active phase during highly exothermic reactions (like the hydrocarbon oxidation) requires thorough spadework from the experimentalist.

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