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Dynamic behaviour of Ni-containing catalysts during partial oxidation of methane to synthesis gas

Yu.P. Tulenin, M.Yu. Sinev*, V.V. Savkin, V.N. Korchak

Semenov Institute of Chemical Physics, Russian Academy of Sciences, 4 Kosygin Street, Moscow 119991, Russia

Abstract

Complex dynamic phenomena—oscillations and temperature waves—are observed during partial oxidation of methane to synthesis gas over Ni-containing metal catalysts (Ni metal foam and chromel–alumel thermocouple). Kinetic analysis of oscillatory process shows that a substantial amount of oxygen and carbon is stored and evolved by catalysts during the cycle. A sharp splash of activity is observed when amounts of stored oxygen and carbon are minimal. It was concluded that the oscillatory behaviour could be due to a difference in the activities of C- and O-covered and clean metal. A "direct" mechanism of CO and H_2 formation without intermediate total oxidation is more probable than a "sequential" one.

Keywords: Methane; Partial oxidation; Synthesis gas; Oscillations; Nickel; Catalysts

1. Introduction

The analysis of dynamic behaviour, including transition processes and self-oscillations, gives valuable information about the intrinsic mechanisms of catalytic reactions [1,2]. Recently we have observed a synergistic behaviour and reaction rate oscillations during methane oxidation in a combined catalytic bed containing oxide catalyst (mixed Mg–Nd oxide) and metal wire (Ni–Cr alloy) [3–5]. Such dynamic phenomena are accompanied by a shift in selectivity from methane coupling products (C_2-hydrocarbons) formed over oxide catalyst alone to synthesis gas ($CO + H_2$) produced in a binary oxide–metal system. Later, similar dynamic phenomena were observed by other authors over Ni metal catalysts without oxide components simultaneously present in the reactor [6,7]. Although the shape of oscillation curves in both cases are very similar, it is important to notice that in the conditions where oscillations were observed in mixed oxide–metal system (relatively low temperatures and flow rates), no reaction over a low surface area metal component taken alone could be detected [3,4]. This strongly suggested that methane activation takes place over the surface of oxide component and some intermediates (likely free methyl radicals) further react over the surface of metal forming final products. Namely the process localised on the metal surface is responsible for the complex dynamic behaviour of the system [5]. Since at higher temperatures similar dynamic phenomena can be observed over Ni-containing catalyst alone [6,7], it is very likely that in these conditions methane can be activated over low surface area metals and following reaction steps proceed over the same surface in the same way as in mixed oxide–metal systems.

These observations can shed light upon the mechanism of methane partial oxidation to synthesis gas, which is still under discussion. Two alternative mechanisms of carbon monoxide and hydrogen formation during methane oxidation with molecular oxygen are extensively discussed in literature (see, for instance, a review in [8]):

(i) "direct"—CO and H_2 are formed as primary products from methane and oxygen;
(ii) "indirect" or "sequential"—methane is first oxidised to CO_2 and water, and then undergoes two endothermic reforming reactions with these primary products.

Justified notions about the reaction pathways may be derived from the "conversion–selectivity" relationships, from the analysis of temperature profiles along the reactor axis

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* Corresponding author. Tel.: +7-95-939-7547; fax: +7-95-938-2156.
E-mail address: sinev@center.chph.ras.ru (M.Yu. Sinev).

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(as it is done, for example in [9]), from experiments with isotope-labelled reactants [10–12]. If the process proceeds in an oscillatory regime, additional information can be obtained by the analysis of reaction kinetics on a short-time scale determined by a characteristic time of oscillations. In particular, valuable information can be obtained from instantaneous material balance and correlation between different parameters of the system under study (such as concentrations and temperatures) varied in a course of oscillatory cycle. The latter approach is used in this paper, where we present new data obtained over low-surface area Ni-containing catalysts (metal Ni foam and Ni–Cr alloys) active in partial oxidation of methane to synthesis gas and displaying the complex dynamic behaviour in a wide range of reaction conditions. A possible mechanism of the appearance of oscillatory behaviour will be also discussed.

2. Experimental

2.1. Catalysts

Two types of low surface area Ni-containing catalysts were used in this work:

- bulky metal nickel foam (0.16 g, ∼5 mm length);
- Ni–Cr alloys.

In the latter case catalytic reaction proceeded on the tip of a chromel–alumel thermocouple which simultaneously played a role of a temperature-sensitive element.

2.2. Reactor and analysis of gas mixtures

Experiments were carried out in a quartz flow reactor (3.5 mm i.d.). Concentrations of components of the reaction mixture were measured by an on-line mass-spectrometric (MS) analysis. Gas probe leaked into the ionisation chamber of the RIBER QMM17 mass-spectrometer through a quartz diaphragm placed right after the catalyst layer and metal capillary with differential pumping. The sampling system provided with a high temporal resolution (better than 0.1 s). In this work we used methane- and oxygen-rich gas mixture (75:20) with 5% of argon added as an internal standard for an MS-analysis.

2.3. Temperature

In this work we used a heating system similar to that described in [4]. It provides with a very uniform temperature profile along the catalyst bed and a sharp decrease of temperature before and after the catalyst. This enables to diminish the probability of side processes in pre- and post-catalytic void volumes. When reaction was carried out over a tip of chromel–alumel thermocouple, the latter was simultaneously used to permanently record a reaction temperature. In the case of bulky Ni-foam catalyst, temperature was measured and recorded using a chromel–alumel thermocouple attached to a front layer of the catalyst.

3. Results

3.1. Reaction over a chromel–alumel thermocouple

At relatively low flow rates of gas mixture (<20 ml/min) methane oxidation is observed at ambient furnace temperatures above 700 °C; total oxidation products (CO_2 and water) are predominantly formed. At increasing flow rate CO and H_2 appear in the reaction mixture and the process transfer into an oscillatory regime. Period of oscillations sharply decreases at increasing gas flow rate and ambient furnace temperature. A typical example of variations of reaction parameters (temperature and gas concentrations) is given in Fig. 1. As can be seen, the maximum methane consumption corresponds to the maximum rate of temperature growth. Oxygen conversion has a two-peak shape: the first maximum coincides with that on methane conversion curve and the second (more intense)—with the maximum temperature. Product concentrations and temperature rise simultaneously, but more detailed features differ from one product to another. CO and hydrogen demonstrate very similar behaviour: the main maximum in their concentrations corresponds to the maximum rate of temperature growth. The second (lower) maximum nearly coincides with the maximum on the temperature curve. CO_2 formation also has a two-peak character, but in this case peak altitudes are nearly the same. As to the water formation curve, it has a single maximum, but its shape is likely to suffer from the retention in the sampling system, which lowers the temporal resolution.

Fig. 2 demonstrates how instantaneous carbon and oxygen balances correlate with temperature variations during one cycle of oscillations. A slightly pronounced broad minimum on “C-balance versus *t*” curve corresponds to the most intense methane consumption and suggests that in this process carbon is partially stored by the catalyst. Maximum temperature corresponds to the most intense elimination of carbon to the gas phase and the maximum rate of oxygen consumption. Whereas C-balance curve demonstrates practically no hysteresis, the “O-balance versus *t*” curve consists of two segments. The upper one corresponds to a “heating” phase of the cycle and reflects the fast formation of carbon oxides at intermediate temperatures (curve maximum) followed by the most intense oxygen consumption (curve minimum); the latter coincides with the maximum on the temperature curve. A smooth “cooling” segment reflects a drop in the rate of the overall process.

The data of Fig. 1 enables to calculate the amount of each element (Δn), e.g. carbon and oxygen, stored in the catalyst within a unit time of reaction:

$$\Delta n = \frac{W\{nC - \sum(\nu_i C_i)\}}{22\,400} \qquad (1)$$

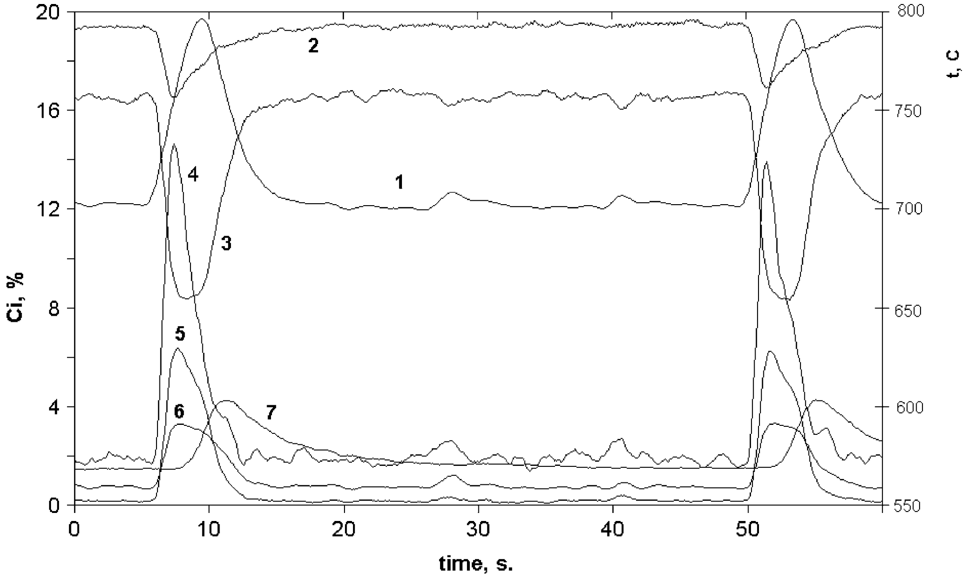

Fig. 1. Typical shape of temperature and concentration oscillations over a chromel–alumel thermocouple: ambient furnace temperature 750 °C, initial mixture CH_4:O_2:Ar = 75:20:5, flow rate 40 ml/min; 1: temperature; 2: CH_4 (0.3×); 3: O_2; 4: H_2; 5: CO; 6: CO_2; 7: H_2O.

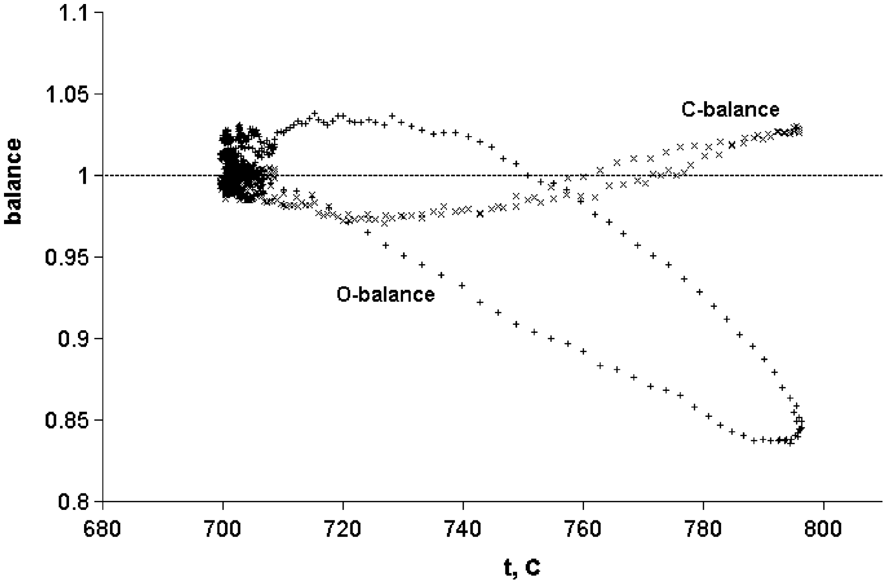

Fig. 2. Carbon and oxygen balances as functions of temperature of chromel–alumel thermocouple during methane oxidation in the conditions of Fig. 1.

where W is the flow rate (ml/s), ν the number of atoms of certain element in a reactant molecule, C the mole fraction of this reactant in the feed gas, ν_i the number of atoms of this element in a product i molecule, C_i the mole fraction of this product in the reaction mixture.

The amount of a certain element stored in the catalyst (N_i) can be calculated by summing Δn values for a given period. The results of such calculations shown in Fig. 3 demonstrate that oxygen storage in the catalyst exceeds by far the storage of carbon and that the maximum in oxygen storage corresponds to the minimum in carbon content in the sample. The maximum amount of oxygen stored in the catalyst within one cycle is about 4×10^{18} atoms. This number exceeds by far the number of atoms on the surface of the thermocouple tip and corresponds to a substantial degree of bulk metal oxidation (about 10%).

3.2. Reaction over a Ni-foam catalyst

General features of the reaction over a Ni-foam are qualitatively very similar to the above described. However, because of much bigger size of this sample, the amounts of stored carbon and especially oxygen are much greater (see Fig. 4). During one period of oscillations, 4.1×10^{-5} g at. or 2.5×10^{19} atoms of oxygen are stored and eliminated by the catalyst, which corresponds to 1.5% of Ni atoms in the catalyst bulk. In general, the process over this catalyst is more complex, this is why the following discussion is based

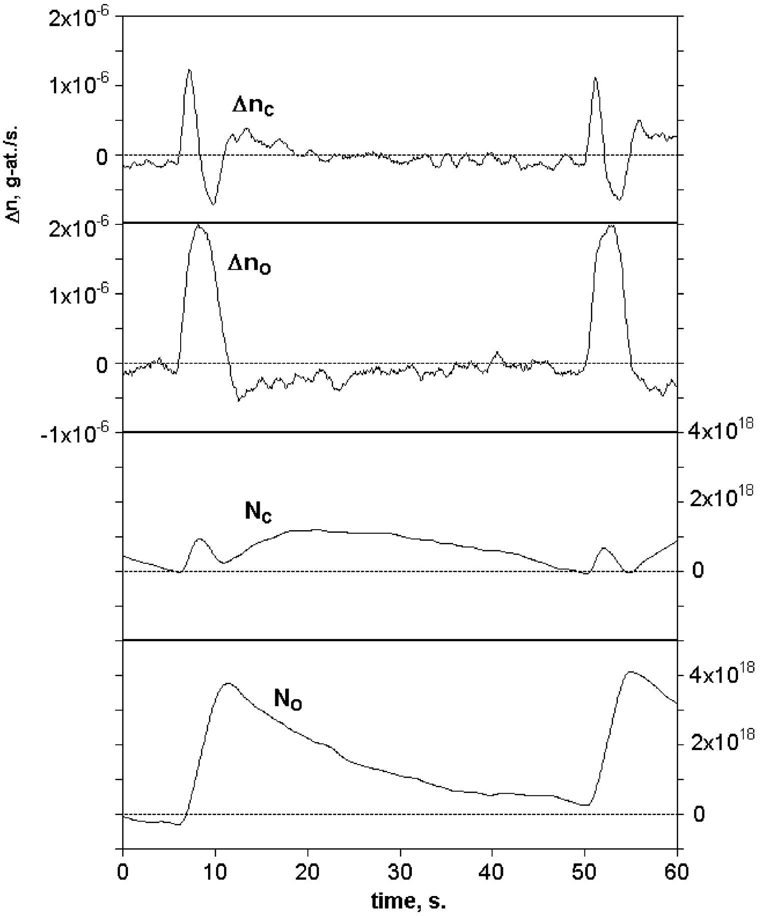

Fig. 3. Instantaneous C- and O-balance variations in the oscillatory regime (conditions of Fig. 1).

mainly on the data obtained with a chromel–alumel thermocouple.

4. Discussion

Mechanisms of self-oscillations in heterogeneous oxidative catalysis are widely discussed in literature (see for instance [1,2]). One possible reason for the appearance of such behaviour is a big difference in the catalytic performance of the solid in different states. The comparison of the data given in Figs. 1 and 3 indicates that the highest rate of methane consumption corresponds to the lowest oxygen and carbon content in the catalyst. This state is also the most active in hydrogen and CO formation. As the degree of catalyst oxidation increases, the formation of these two products decreases. On the other hand, the rate of water formation well correlates with the content of oxygen in the catalyst. As to the formation of CO_2, it has a two-peak character. The first maximum corresponds to the highest rate of methane consumption, the second—to a substantially increased degree of catalyst oxidation.

Total oxidation products—CO_2 and water—continue to form during the period of low activity when the contents of both oxygen and carbon in the catalyst are significant. It is very likely that during this period they form at the expense of coke deposit interaction with stored oxygen. Simultaneously, slow methane decomposition and carbon deposition are accompanied with the formation of hydrogen. Since CO practically does not form during this period, no indication of interaction between deposited carbon and CO_2 is seen. The latter suggests a big difference with dry reforming of methane, which can proceed via the decomposition of methane, formation of carbon deposits and their further interaction with gaseous CO_2 [13].

As the contents of both oxygen and carbon decrease and liberate the metal surface, the rate of methane consumption sharply increases, and the cycle repeats. It is important to notice that no indication for the sequential formation of CO and hydrogen is found. Moreover, all the regularities observed in both periods of high and low activity fit in well with a direct mechanism. Earlier the conclusion about a higher probability of “direct” mechanism was derived from the results of isotope-labelling experiments [11,12].

One more remark should be made on the dynamic regime over a bulky Ni-foam catalyst. It was observed that methane oxidation is often associated with temperature waves moving along the catalyst/reactor axis. It is very likely that

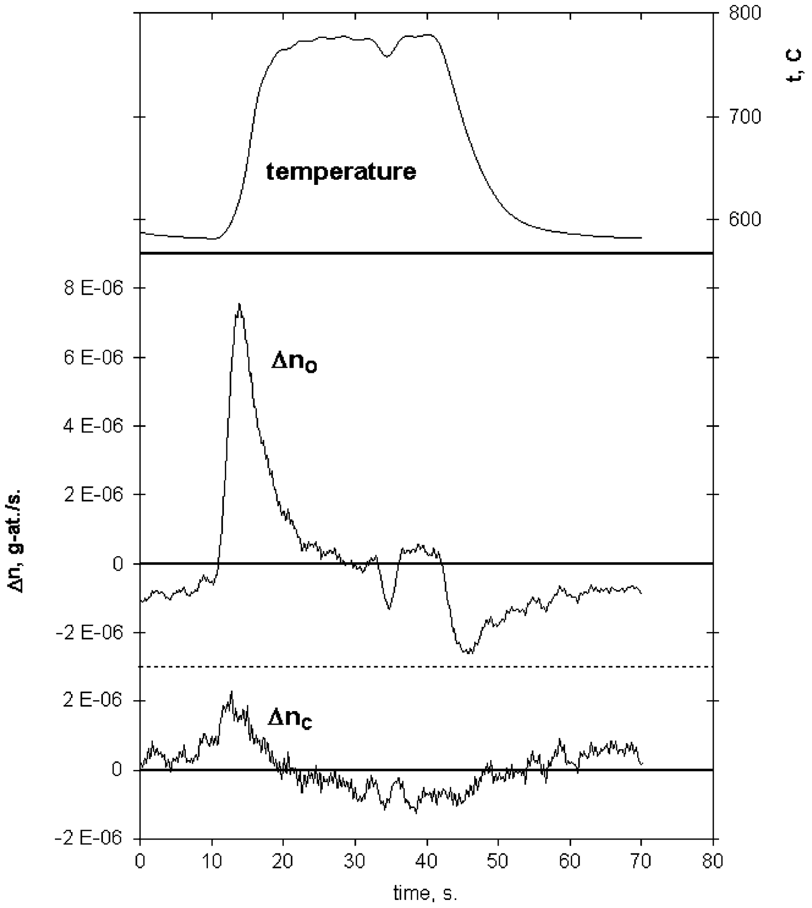

Fig. 4. Temperature and instantaneous C- and O-balance variations in the oscillatory regime of methane oxidation over a metal Ni-foam catalyst (0.16 g); ambient furnace temperature 600 °C, initial mixture CH_4:O_2:Ar = 75:20:5, flow rate 80 ml/min.

oscillations of temperature measured by a thermocouple placed in the front layer of the catalyst just reflect in some complex manner this wave process which involves the whole bulk of catalyst. Moreover, since the thermocouple itself can act as a catalyst, it is difficult to measure the catalyst temperature with high precision and spatial/temporal resolution. This is why a more attention has to be paid to the selection of an appropriate technique for temperature measurements. In particular, we plan to use a dynamic photometry specially developed for this application.

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