

Oscillations in Partial Oxidation of Methane to Syngas over Supported Mixed Oxides Promoted with Pt

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Abstract

Ni, Pt, lanthanum nickelate with and without Pt supported on corundum carrier either pure or promoted with $\text{CeO}_2\text{-ZrO}_2$ were tested in partial methane oxidation (POM) to synthesis gas under conditions (high temperature, short contact time, highly diluted gas mixture, small catalyst grains) providing studying of the intrinsic kinetics. The phase composition and reducibility of catalysts were characterized with XRD and TPR technique. The influence of catalyst composition on the catalyst performance has been studied. The self-sustained oscillations of methane conversion and products concentration have been observed. The nature of those oscillations is discussed taking into account the intrinsic properties of the catalysts clarified with TPR and XRD.

INTRODUCTION

The catalytic partial oxidation of methane (POM) to syngas at short contact times is an alternative process to the conventional steam reforming of natural gas [1–5]. Testing of the catalysts under atmospheric pressure revealed good yields and selectivity to syngas in the case of precious metal-containing (first of all, Rh-containing) monolithic catalysts [3]. However, at high pressures syngas yield drops due to thermodynamic limitations and radical gas-phase reactions [4]. To minimize the effect of the gas-phase reactions, the process is to be carried out under kinetic not thermodynamic control. To obtain a high methane conversion at short contact times and kinetically controlled high yields of syngas at high pressures, the catalysts providing a high rate of methane transformation by the route including methane pyrolysis – selective carbon oxidation into CO – are to be designed. The problem include the design of the metal active component providing efficient methane decomposition and selection of the oxide support with enhanced bulk and surface oxygen mobility [6, 7].

Supported lanthanum nickelates and cobaltites of the perovskite type promoted with small amounts of precious metals were shown to be more active and stable catalysts in this process than supported precious metals [8]. A high oxygen mobility in fluorite-like $\text{CeO}_2\text{-ZrO}_2$ solid solutions helps to ensure an efficient performance of Pt supported on monolithic corundum in POM [9]. The catalysts in those experiments were tested under non-isothermal conditions due to a high methane concentration used, monolithic shape of catalysts *etc.* In order to develop highly effective POM catalysts favoring direct methane conversion into syngas, it is necessary to obtain data characterizing the intrinsic activity of active components under conditions as close as possible to industrially relevant ones (high temperatures, short contact times).

In this work the activity in POM of Ni, Pt, lanthanum nickelate with and without Pt supported on corundum carrier either pure or promoted with $\text{CeO}_2\text{-ZrO}_2$ was studied under conditions (high temperature, short contact time, highly diluted gas mixture, small catalyst grains) providing obtaining of intrinsic kinetic data.

The phase composition and reducibility of catalysts were also characterized with XRD and TPR.

EXPERIMENTAL

The catalysts containing Pt, Ni and LaNiO₃ either pure or promoted with Pt were prepared by incipient wetness impregnation of microspheric α -Al₂O₃ (100 μ m diameter) with required salt solutions (Table 1). First Ce-Zr oxide was deposited on α -Al₂O₃ from the solutions of Ce(NO₃)₃ and ZrOCl₂. After the impregnation, samples were dried and calcined at 900 °C in air. Active components were then supported using solutions of La and Ni nitrates, H₂PtCl₆, and samples thus obtained were dried and calcined once more.

XRD spectra of catalysts were recorded using HZG-4C spectromoter Freiburger Präzisionstechnik with monochromatic CuK α irradiation. The mean crystallite sizes of Ce-Zr mixed oxide, LaNiO₃, NiO and Pt were determined from XRD line broadening measurements using Scherrer equation. The reflexes at $d = 1.9065$ and 1.7027 Å corresponding to (202) and (211) planes of LaNiO₃ (No. 34-1181,

JCPDS-ICDD) were used for estimation of LaNiO₃ lattice parameters and the average crystallite sizes. The lattice parameters and the average crystallite size of Ce-Zr mixed oxide were determined from the reflexes at $d = 1.83094$ Å corresponding to (202) CeZr solid solution planes.

Before TPR experiments, the samples were heated in oxygen at 500 °C for 30 min and then cooled to room temperature. After this oxygen was successively changed for argon and the feed containing 10 % vol. H₂ in Ar. The feed flow rate was 40 ml min⁻¹. The heating rate from room temperature to 900 °C was 10 °C min⁻¹. During the experiment H₂O was frozen out at -80 °C. The hydrogen concentration was determined using the thermal conductivity detector.

The catalysts were tested in POM at atmospheric pressure in a continuous flow quartz reactor with 10 mm inner diameter. 0.01 g of the catalyst diluted with quartz powder (0.25–0.5 mm) was placed between two disks of “Buran” foam silica. The temperature of the catalytic bed was measured by a thermocouple placed outside the reactor. Before testing, the catalysts were activated using two procedures. According to the first one, the samples were oxidized for 1 h at 900 °C in the oxygen flow.

TABLE 1
XRD data

Catalyst	Chemical composition	Phase composition	Lattice parameters, Å		Crystal size, Å
			<i>a</i>	<i>c</i>	
ZC-A	Zr _{0.8} Ce _{0.2} /α-Al ₂ O ₃	Ce _{0.8} Zr _{0.2} O ₂ CSS*	5.182		125
P-ZCA	0.4 % Pt/Zr _{0.8} Ce _{0.2} /α-Al ₂ O ₃	Ce _{0.8} Zr _{0.2} O ₂ CSS Pt	5.179		105 250
LN-A	LaNiO ₃ /α-Al ₂ O ₃	LaNiO ₃ NiO	5.366	6.579	220
LN-ZCA	LaNiO ₃ /Zr _{0.8} Ce _{0.2} /α-Al ₂ O ₃	Ce _{0.8} Zr _{0.2} O ₂ CSS LaNiO ₃ NiO	5.182 5.371	6.592	120 170 <50
LNP-A	0.2 % Pt + LaNiO ₃ /α-Al ₂ O ₃	LaNiO ₃	5.382	6.629	175
LNP-ZCA	0.2 % Pt + LaNiO ₃ /Zr _{0.8} Ce _{0.2} /α-Al ₂ O ₃	Ce _{0.8} Zr _{0.2} O ₂ CSS LaNiO ₃ NiO-traces	5.188 5.383	6.625	90 100
N-ZCA	1.3 % Ni/Zr _{0.8} Ce _{0.2} /α-Al ₂ O ₃	Ce _{0.8} Zr _{0.2} O ₂ CSS NiO	5.179		110 50

*CSS – cubic solid solution.

In the next one, the catalysts were oxidized for 1 h at 700 °C in the oxygen flow, then it was switched to He followed by the feed 30 % H₂ in He. Simultaneously, the temperature was raised to 900 °C so that the catalysts were reduced for 30 min. The catalysts were tested then at 900 °C and contact times $2 \cdot 10^{-3}$ and $30 \cdot 10^{-3}$ s. The methane content in the feed gases was 1 % vol. The oxygen content varied within 0.01–0.5 % vol. range (helium balance). The reaction products were analyzed by the GC. The methane conversion and selectivity to products were calculated on the basis of carbon numbers of the methane reacted. Carbon balances were within the limit of ± 5 %.

RESULTS AND DISCUSSION

XRD data

Some catalyst characteristics are presented in Table 1. The Ce_{0.2}Zr_{0.8}O₂ oxide supported onto corundum is a solid solution of the cubic structure. For all samples, their lattice parameters are nearly constant whereas the average crystallite size is reduced for samples containing Pt. Supported lanthanum nickelate either pure or containing Pt corresponds to perovskite of the hexagonal structure which predominates in all catalysts. The broad lines of low intensity corresponding to NiO are observed in XRD patterns of LN-A and LNP-ZCA samples testifying the presence of some amount of small NiO particles. The diffraction lines of Pt were not observed for LNP-A and LNP-ZCA samples probably as a result of both low Pt concentration and its incorporation into the perovskite structure.

The lattice parameters of supported LaNiO₃ (see Table 1) are different from those of a bulk perovskite (No. 34–1181, JCPDS-ICDD), thus evidencing that the structure of supported perovskite is distorted due to its interaction with the support. The addition of Pt results in the increase of perovskite lattice parameters and decrease of the average perovskite crystal size. These alterations can be due to Pt incorporation into the perovskite lattice. For catalysts supported on corundum promoted with Ce–Zr oxide, the variation of the perovskite

lattice parameters is more pronounced depending on the presence of Pt as well. The parameter *c* of pure supported LaNiO₃ phase is bigger for LN-ZCA sample as compared with that for LN-A, whereas perovskite lattice parameters of LNP-ZCA and LNP-A samples containing Pt are the same. Corundum modification by Ce–Zr oxide favors a higher perovskite dispersion (see Table 1), both for pure (LN-ZCA) or Pt containing system (LNP-ZCA).

Temperature-programmed reduction

The TPR data are presented in Fig. 1. TPR spectra for supported Ce_{0.2}Zr_{0.8}O₂ show three peaks of hydrogen consumption at 312, 440 and 530 °C. The peaks are relatively weak indicating a low total hydrogen uptake. In the spectrum of P-ZC-A an intense peak at 325 °C appears evidencing that Pt facilitates the reduction of Ce–Zr oxide. Spectra for N-ZC-A show three peaks at 235, 470 and 840 °C. For LaNiO₃ supported on pure corundum (LN-A), a weak peak at ~350 °C and two high intensity peaks at 530 and 890 °C are observed. The spectrum of LN-ZCA also shows three peaks

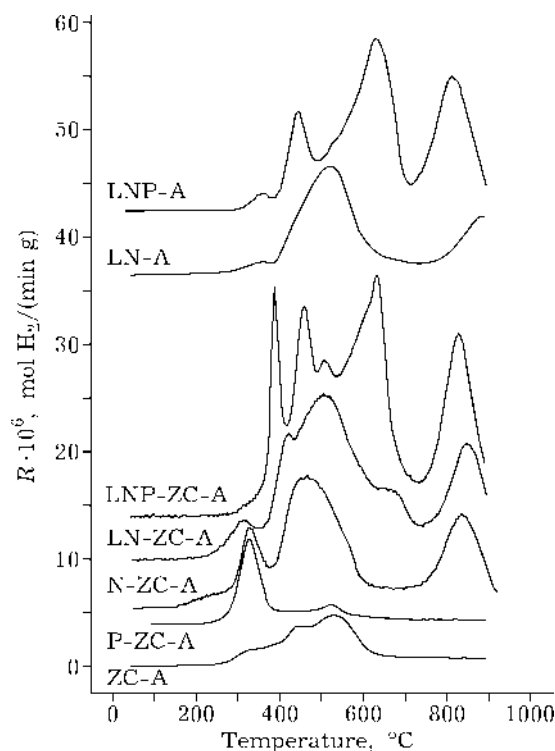


Fig. 1. TPR profiles of the catalysts.

shifted to lower temperatures. In addition, shoulders at 420 and 670 °C appear. Hence, $\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$ sublayer facilitates the reduction of LaNiO_3 . Such a different behavior of LaNiO_3 perovskite supported on $\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2/\alpha\text{-Al}_2\text{O}_3$ correlates with the increase of the lattice parameter c indicating the influence of $\text{Ce}_{0.2}\text{Zr}_{0.8}\text{O}_2$ on the perovskite structure.

Addition of Pt strongly affects the TPR profiles of LNP-A and LNP-ZC-A samples. The most pronounced changes are observed at temperatures below 700 °C. For LNP-A, intensive peaks at 450 and 650 °C appear, while the high temperature peak is shifted by 70 °C to low temperature as compared with that for LN-A sample. For LNP-ZCA, the spectrum is more complicated as compared with that for LNP-A: three peaks are observed at temperature below 550 °C, whereas the position of the high

temperature peaks at 650 and 820–850 °C is unchanged. In the case of Pt containing catalysts, Ce–Zr oxide favors their reduction at temperature below 600 °C.

Catalytic activity

The activity of catalysts depends both on the catalyst composition and the procedures of samples pretreatment before the kinetic study.

Data on catalytic activity of oxidized N-ZCA and LNP-ZCA are presented in Figs. 2, 3. The initial activity of both catalysts after the first 1–2 min of contact with the reaction mixture is rather low (see Fig. 2, 3): methane conversion is 10–18 % and only traces of CO are detected in the reaction products. It is known

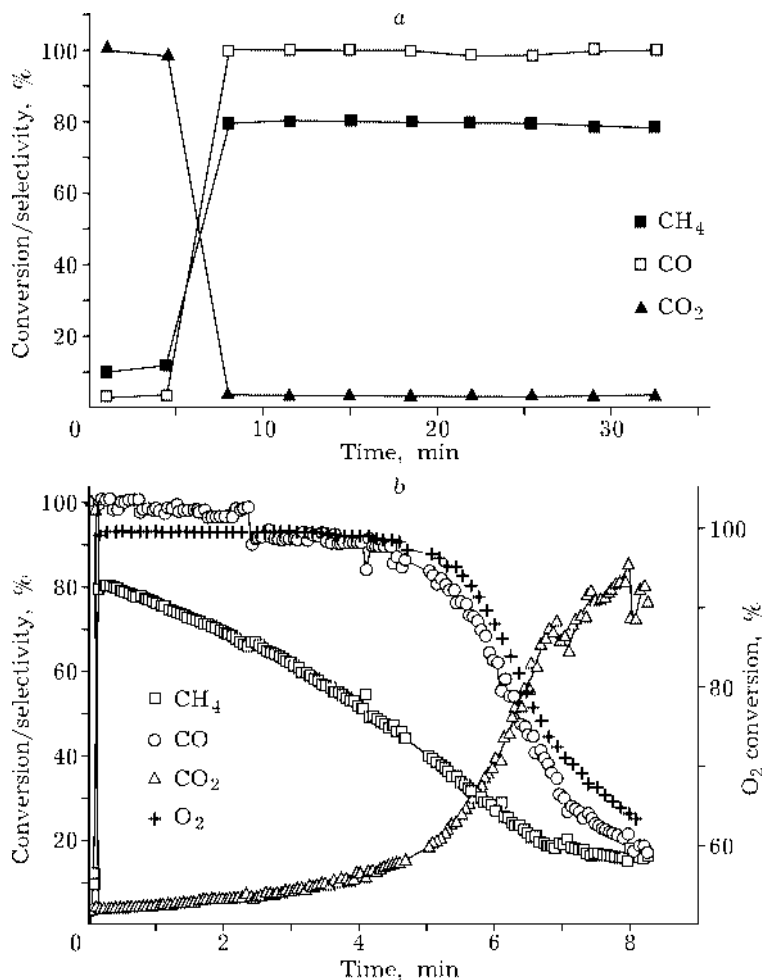


Fig. 2. Conversion of methane and oxygen, CO and CO₂ selectivities for preoxidized N-ZC-A: a – at the initial period of testing; b – during 8 h. Here and in Figs. 3–5: 900 °C, contact time $2 \cdot 10^{-3}$ s, 10 000 ppm CH₄, 5000 ppm O₂, helium – balance.

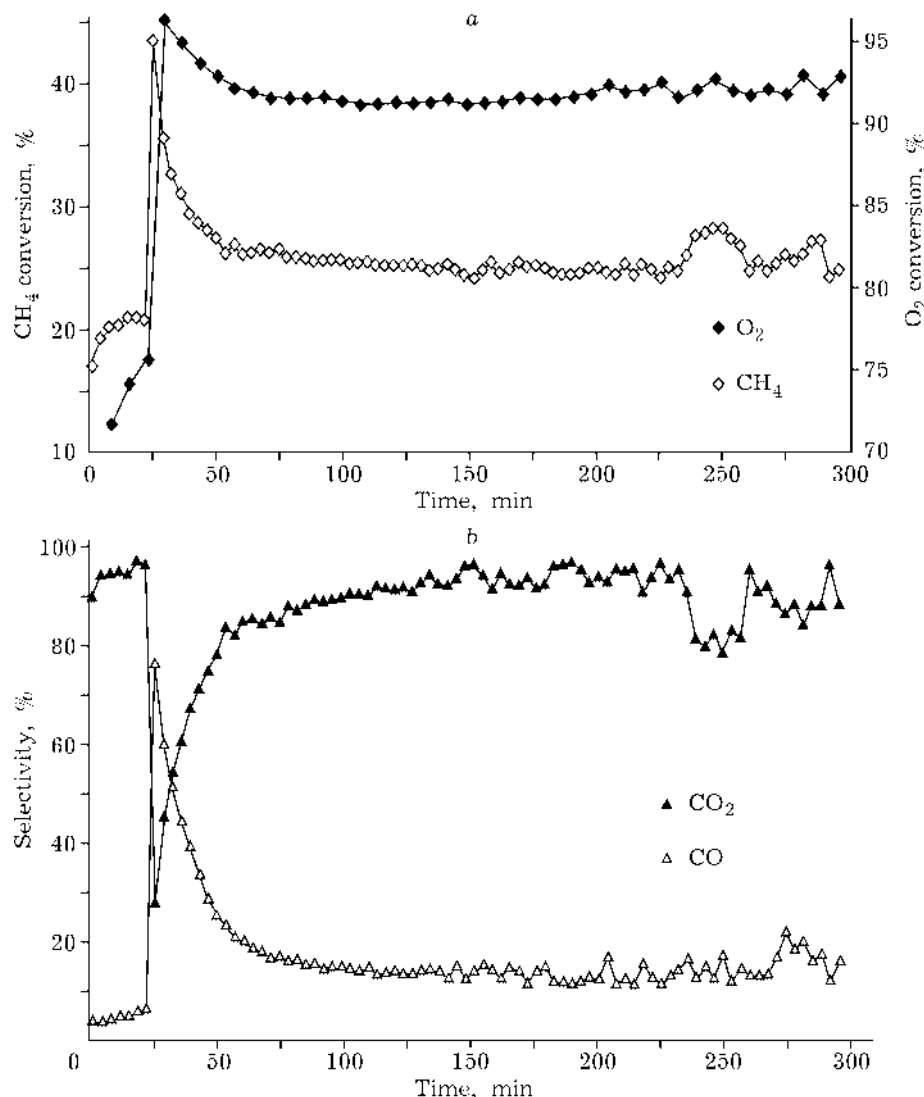


Fig. 3. Conversion of methane and oxygen (a), CO and CO₂ selectivities (b) for preoxidized LNP-ZC-A. Designation: see Fig. 2.

that oxide nickel species catalyze only non-selective methane oxidation (combustion) [11]. For both catalysts, the sharp increase in conversions and selectivity to syngas is observed after an induction period, then they decrease with time. The induction period is determined by NiO reduction to metal Ni having a high POM activity and selectivity [11,12] and depends on the active component phase composition (see Table 1). An induction period is longer for LN-ZCA and LNP-ZCA samples containing LaNiO₃ perovskite as compared to N-ZCA sample containing only NiO, due to worse reducibility of the former samples under reaction conditions (a low methane concentration, an extremely short contact time). The maximum activity is higher for N-ZCA (see Fig. 2), a slight

decrease of N-ZPA activity may be attributed to the fact that whole nickel is in the form of easily reducible NiO particles. For LNP-ZCA some oscillations of reagents conversion and selectivity to CO and CO₂ appear after 150 min staying in the feed (see Fig. 3). These oscillations with a low amplitude and a short periodicity take place only for oxidized LNP-ZCA, and they are not observed over catalysts without Ce-Zr-O secondary layer. Similar oscillations in the reaction of partial methane oxidation into syngas were observed in [13] for Rh/ γ -Al₂O₃ catalyst pretreated with methane.

Complete gas phase oxygen consumption is observed for all catalysts indicating strong catalyst reduction under the reaction conditions. So, it was very interesting to test the catalytic

TABLE 2

The conversion of methane, oxygen and selectivity to CO and CO₂ over reduced catalysts

Catalyst	Conversion*, %				Selectivity*, %			
	CH ₄		O ₂		CO		CO ₂	
	1	2	1	2	1	2	1	2
P-ZCA	28	30	95	92	24	13	76	87
N-ZCA	44	15	99.7	52	65	10	35	90
LN-ZCA	56.5	17	99.7	52	84	29	16	71
LNP-ZCA	28	25	76	67	61	40	39	60

Note. Temperature 900 °C, contact time $2 \cdot 10^{-3}$ s, 10 000 ppm CH₄, 5000 ppm O₂, helium – balance. Before activity testing the catalysts were reduced in the hydrogen flow (*vide supra*).

*1 – the initial activity, 2 – after 3 h of testing.

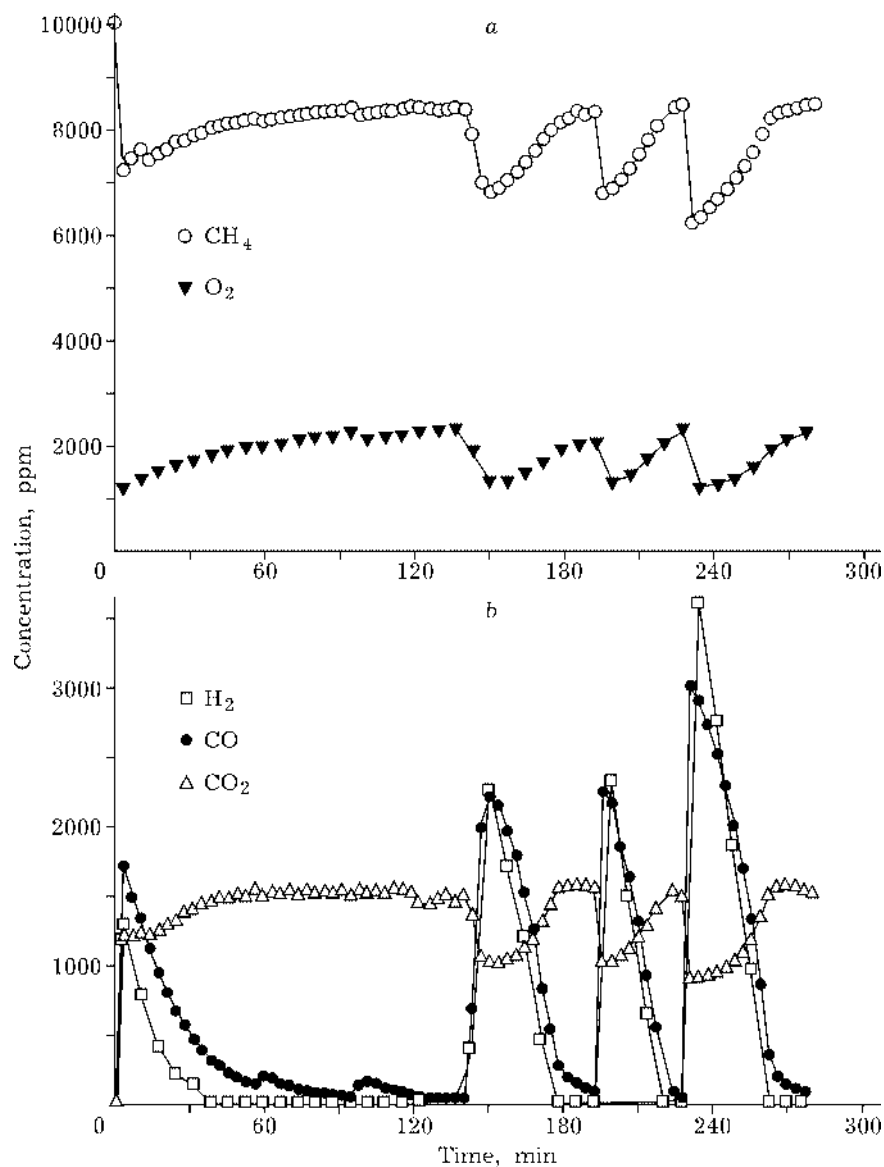


Fig. 4. Oscillations of the reagents (a) and products (b) concentrations over prerduced LNP-ZCA. Designation: see Fig. 2.

activity of prerduced catalysts. Kinetic data obtained over prerduced catalysts in the first few seconds and after 3 h staying in stream are presented in Table 2. Initially, LN-ZCA catalyst is the most active in syngas formation, but its activity decreases significantly after 3 h of the catalytic run. The addition of Pt leads to the increase of perovskite stability in the syngas production. The state of prerduced catalysts changes with time-on-stream as in the case of oxidized samples. These changes are manifested in the decrease of the catalytic activity, the gas phase oxygen consumption and H_2/CO ratio in the reaction products. In the case of prerduced LNP-ZCA, stable oscillations in methane, oxygen (Fig. 4, a) and products concentration (see Fig. 4, b) are observed as well. Note that oscillations appear at the H_2/CO ratio close to 1 as in the case of oxidized LNP-ZCA catalyst. In contrast to the oxidized catalyst, these oscillations are characterized by a higher amplitude and a lower frequency (see Figs. 3, 5). Period of oscillations is rather long (about 40–50 min). The amplitude of these “low frequency” oscillations increases with time. Some remarks concerning the reason of oscillations could be made on the bases of the oxygen uptake analysis in the system “catalyst–gas phase (reagents and products)”. The consumption of oxygen by the catalyst is presented in Fig. 5, c (solid line). After about one hour of the experiment, the concentrations of CO and hydrogen are practically close to zero (see Fig. 4, a). At that time, CO_2 is the main reaction product, the amount of oxygen consumed by the catalyst is close to 1 mmol O_2 per gram of catalyst (see Fig. 5, c). Then oxygen consumption by the catalyst stops. Just in that moment the first oscillation arises (see Fig. 5). The subsequent oscillations proceed at the moment when the catalyst releases or absorbs about 1 mmol of molecular oxygen. According to TPR data, the oxygen capacity of Ce–Zr–O solid solution is comparable with this value. Note, that “low frequency” oscillations are observed only in the case of catalysts containing Ce–Zr–O secondary support. The coincidence of these values and the latter fact permit us to suggest that “low frequency oscillations” observed are caused by the changes in the catalysts state associated

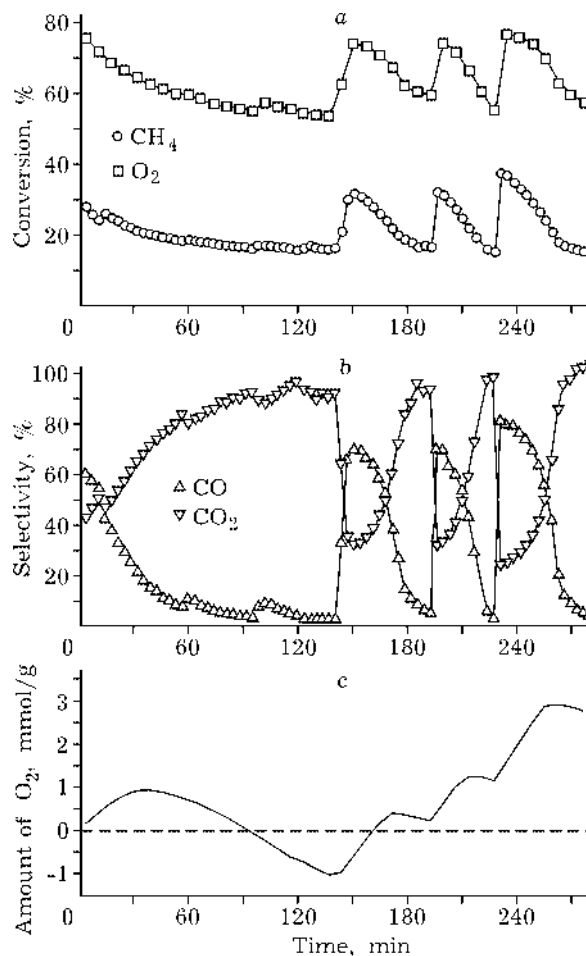


Fig. 5. Oscillations of conversions (a) and selectivities (b) over prerduced LNP-ZCA: c - amount of oxygen consumed by the catalyst. Designation: see Fig. 2.

with the oxygen transport through the Ce–Zr–O secondary layer during the reaction.

CONCLUSIONS

The partial oxidation of methane to synthesis gas over supported mixed oxides (La, Ni) with Pt has been studied in isothermal conditions at millisecond contact times. In all catalysts supported lanthanum nickelate phase either pure or containing Pt predominates and corresponds to perovskite of the hexagonal structure with modified lattice parameters. The redox properties of catalysts depend on the presence of Pt and CeO₂–ZrO₂ solid solution.

The initial intrinsic activity of catalysts depends on both the catalysts composition and the procedures of samples pretreatment before the kinetic study. The addition of Pt and

Ce-Zr oxide leads to the increase of the catalysts stability.

For the catalysts containing Ce-Zr mixed oxide, self-sustained oscillations of the reaction rate and selectivity are observed. The oscillations observed for preoxidized Pt-LaNiO₃/Ce-Zr-O/Al₂O₃ catalysts have a low amplitude and a short periodicity. The "low frequency" oscillations observed only for prereduced Pt-LaNiO₃/Ce-Zr-O/Al₂O₃ seem to be related to the oxygen transport in the Ce-Zr-O secondary layer. The difference in the character of oscillations over oxidized and reduced catalysts can be due to their different degree of reduction.

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