Catal Lett (2007) 119:339–345
DOI 10.1007/s10562-007-9241-3

Oscillatory Behaviour During Ethane Oxidation Over Nickel and Cobalt Catalysts

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Received: 14 June 2007 / Accepted: 15 August 2007 / Published online: 7 September 2007

Abstract Oscillatory behaviour during ethane oxidation over a nickel foil and a cobalt foil has been studied using on-line mass-spectrometry and video recording of the catalyst surface colour. It was demonstrated that during the oscillatory behaviour, periodic transitions of the catalyst surface from an oxidised state to a reduced state occurred together with a variation of the catalyst temperature. Simultaneous measurements of gas phase concentrations revealed that mostly CO_2 was produced over the oxidised state, while CO and H_2 production rates reached their maxima over the completely reduced surface. The comparison of the observed oscillations with known oscillations during methane oxidation over nickel and cobalt foils has been done. It was shown that the higher reducing ability of ethane was the reason of an increase of the frequency of the oscillations over both catalysts and a significant decrease of the temperature range of the oscillations over the cobalt foil.

Keywords Oscillations · Ethane oxidation · Cobalt catalysts · Nickel catalysts

1 Introduction

Self-sustained reaction rate oscillations and spatial concentration structures on catalyst surface represent excellent examples of self-organisation in heterogeneous catalytic systems far from equilibrium. The study of these phenomena is one of the most exciting fields in heterogeneous catalysis and more than 65 oscillating heterogeneous catalytic systems are known today [1]. Recently an oscillatory behaviour during methane oxidation has been discovered and investigated over Ni [2–6] and Co catalysts [7, 8]. It was suggested that the oscillatory behaviour during methane oxidation over nickel and cobalt catalysts originated from the periodic oxidation and reduction of the metal catalyst [9]. The application of thermogravimetric analysis (TGA) in combination with on-line mass-spectrometry showed that a significant variation of surface oxygen content (several tens of layers) occurred during the oscillations of methane oxidation over Ni catalysts, verifying the periodic oxidation and reduction of the metal surface [6]. The visual observation of periodic colour changes during the oscillatory behaviour due to the variation of Ni and Co valence provided the additional evidence that oxidation–reduction processes played a crucial role in the origin of the oscillatory behaviour during methane oxidation over these catalysts [6, 8]. Mathematical modelling of the oscillatory behaviour during methane oxidation over Ni catalysts demonstrated that thermokinetic oscillations could arise from periodic oxidation and reduction of the catalyst surface, from the variation of the selectivity of the process and the competition of reactants for free active sites [10].

An oscillatory behaviour over nickel catalysts has been detected also during propane oxidation [11–12]. Gladky et al. observed oscillations in the product concentrations in the temperature range (650–750 °C) similar to the oscillations during methane oxidation over Ni catalysts. The authors suggested that the observed oscillations of the rate of propane oxidation over nickel were accompanied by periodic oxidation and reduction of the catalyst surface. An

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application of in situ thermography had shown that reaction rate oscillations were accompanied with periodic changes of the catalyst temperature [12]. However, authors [12] rejected the thermokinetic nature of the oscillations and no mathematical modelling of the observed dynamic behaviour had been done.

In this paper, we report the first observation of oscillations during ethane oxidation over Ni and Co catalysts. The goal of the paper is to describe the dynamic behaviour during ethane oxidation over Co and Ni foils and to compare the properties of oscillations during oxidation of light alkanes over these catalysts.

2 Experimental

The oscillatory behaviour during ethane oxidation was carried out in a transparent tubular quartz flow reactor (i.d. 6 mm), operated at atmospheric pressure. An electric furnace was made of quartz tube (i.d. 18 mm) with wound nichrome wire. The reactor was inserted into the furnace through its side hole transversely to the furnace axis. This construction allowed the observation of the reactor within the furnace through the open end of the tubular furnace and the recording of the state of the sample surface using a video camera (JVC, Crawley, UK, model GR-D230).

The initial gas mixture (C_2H_6 : O_2 : Ar = 17.5:7.5:1) was supplied at flow rates from 10 to 40 ml/min, regulated by mass flow controller. Small part of the reaction mixture flow was separated at ~20 mm below the catalyst position and directed to a quadrupole mass spectrometer (Pfeiffer, Kingston, ON, Canada, OmniStar GSD 301) via a heated stainless capillary. It should be noted that both CO and C_2H_4 have parent peaks with m/z = 28, which overlap with C_2H_6 fragment peak. Therefore, ethylene concentration was calculated using the peak with m/z = 27 after the subtraction of the intensity of C_2H_6 cracking fragment. CO concentration was calculated using the intensity of m/z = 28 peak after the subtraction of the contributions from C_2H_4 and C_2H_6 peaks.

Studies of the oscillatory behaviour over Ni and Co catalysts revealed that bare chromel–alumel thermocouples could be effective catalysts for methane oxidation, being able to generate oscillatory behaviour in the temperature range from 650 to 730 °C [3, 8]. When using a thermocouple, precautions were taken to avoid ethane oxidation at its surface. A piece of the nickel capillary (diameter of 2 mm, wall thickness of 0.25 mm) was applied to prepare a Ni sample. The ends of chromel and alumel wires were inserted inside the capillary and compressed with the capillary to form the Ni foil sample with the internal thermocouple, allowing measuring the catalyst temperature (T_{cat}). The free ends of the wires were inserted into holes of a ceramic tube and practically had no any contact with the reaction gas. The obtained Ni catalyst was the 0.5 mm thick 4.8 × 3 mm^2 metallic foil.

Two Co foils were used as catalysts. The size of the first sample (Co1) was 7 × 3 × 0.75 mm^3 and the size of the second sample (Co2) was 4 × 4 × 0.16 mm^3. Temperature of Co1 sample was measured by a chromel–alumel thermocouple in a stainless steel shell welded to the sample. The temperature of the reactor (T_r) was measured by a thermocouple on the outer side of the reactor.

3 Results

3.1 Homogeneous Oxidation of Ethane in the Empty Reactor

Homogeneous oxidation of ethane was studied at reactor temperatures (T_r) of 500–700 °C by introducing into the empty reactor a reaction mixture comprising C_2H_6 :O_2 : Ar = 17.5:7.5:1. At T_r lower than 600 °C the rate of homogeneous oxidation was very small. At T_r higher than 600 °C the conversion of oxygen increased rapidly with temperature reaching a value of ~95% at 650 °C. Table 1 demonstrates that under the chosen conditions ethylene and CO were the main carbon-containing products of homogeneous ethane oxidation and only steady state catalytic activity was observed.

3.2 Oscillatory Behaviour During Oxidation of Ethane Over the Ni Foil

Previously, we reported the results of the investigation of oscillations during methane oxidation over Ni catalysts [6]. It was demonstrated that oxidised and reduced states of a Ni foil could be clearly distinguished by visual observations. Under the chosen experimental conditions, the reduced metallic Ni had a shiny, light colour, which turned

Table 1 Effect of temperature on O_2 and products concentrations (%vol.) during gas phase ethane oxidation (C_2H_6 : O_2 : Ar = 17.5:7.5:1, 20 ml/min)

T_r (°C)	O_2	CO	CO_2	C_2H_4	H_2
500	26.3	0.6	0	0.14	0
525	26.2	0.75	0	0.18	0
550	26.1	0.85	0	0.18	0
575	26.0	1.0	0	0.2	0
600	25.8	1.1	0.01	0.25	0
625	25.2	1.3	0.04	0.9	0.01
650	1.05	13	1.9	10	1.0

black after oxidation. As will be shown below the information about the state of a Ni foil during ethane oxidation can be also obtained by the visual observation.

Oxidation of ethane over the Ni foil has been studied at flow rates from 10 to 30 ml/min at T_r temperatures of 500–700 °C (reaction mixture C_2H_6 : O_2 : Ar = 17.5:7.5:1). Table 2 demonstrates the effect of temperature on concentrations of reaction products at a flow rate of 20 ml/min. It can be seen that in T_r temperature range between 500 and 650 °C only steady state catalytic activity was detected. In this temperature range T_{cat} was lower than T_r and the colour of the catalyst surface was black indicating the oxidised state of the catalyst. Table 2 also shows that in this temperature range the main product of ethane oxidation was CO_2. The concentrations of CO and C_2H_4 were lower than those obtained in the empty reactor and the drastic increase of CO and ethylene concentration at 650 °C, which was detected during homogeneous ethane oxidation, was not observed.

Oscillatory phenomena were observed at T_r higher than 660 °C. Figure 1 shows the effect of temperature on the oscillatory behaviour. At T_r of 670 °C oxygen and ethane conversion were still small. Figure 1a demonstrates relaxation oscillations at this temperature with spikes of the reaction rate and the catalyst temperature T_{cat}. However, the average temperature of the catalyst was still lower then T_r. Period of the oscillations was close to 150 s. The system spent more time in the low activity branch of the oscillatory cycle corresponding to the oxidised surface. During the spikes the surface changed rapidly its colour from dark to light indicating the surface reduction. On the reduced surface H_2, CO, CO_2 concentrations sharply increased, while O_2 and C_2H_4 concentrations fell down.

At T_r = 680 °C the average rate of ethane oxidation as well as the intensity of the reaction rate oscillations significantly increased (see Table 2; Fig. 1b), while oxygen concentration decreased to very low values. In the high reactivity phase of the oscillations the catalyst temperature was about 30 °C higher than the reactor temperature. Figure 1b demonstrates the increase of the frequency of the oscillations with the temperature increase. It can be seen that the products CO, CO_2, H_2 were in-phase with one another, whilst being counter-phase with O_2 and C_2H_4.

As the temperature T_r was further increased, the frequency of the oscillations tended to increase and the amplitude to decrease. Table 2 and Fig. 1c show some rise of CO and C_2H_4 concentrations at 690 °C and significant decrease of oxygen concentration down to 1.2–1.3%. Further temperature increase caused the appearance of oscillations with so high frequency that it was practically impossible to detect the oscillatory behaviour by the mass spectrometer. However, visual observations of the catalyst surface allowed to observe high frequency variations of the catalyst colour.

3.3 Oscillatory Behaviour During Oxidation of Ethane Over Co Foils

In contrast to Ni there are three states of cobalt surface with different degrees of oxidation, which can be distinguished by visual observations [8]. TPR and thermogravimetric studies together with visual observations of cobalt catalyst showed that the completely reduced surface had a light metallic colour, while a partially oxidised, black catalyst was identified as CoO. Totally oxidised, grey sample was

Table 2 Effect of temperature (°C) on O_2 and products concentrations (%vol.) during the ethane oxidation over the Ni foil (C_2H_6 : O_2 : Ar = 17.5:7.5:1, 20 ml/min)

T_r	T_{cat}	O_2	CO	CO_2	C_2H_4	The dynamic behaviour
500	450		0	0.34	0	Stationary reaction
550	503		0	0.64	0.05	Stationary reaction
575	530		0	0.8	0.15	Stationary reaction
600	557		0	0.98	0.2	Stationary reaction
625	585		0.04	1.1	0.38	Stationary reaction
635	595		0.04	1.1	0.57	Stationary reaction
650	611		0.14	1.2	1.1	Stationary reaction
660	624		0.34	1.4	1.75	Stationary reaction
670	641	19.75	1.24	3.5	3.46	Oscillations
	636	21.1	0.64	1.75	3.5	
680	713	2.1	7.04	10	8.05	Oscillations
	678	2.6	4.84	5.4	12.85	
690	724	1.2	8.24	7.4	10.75	Oscillations
	715	1.3	6.64	6.1	13.75	
700	739	0.75	9.74	5.6	12.55	Oscillations
	733	0.79	8.44	4.94	14.65	

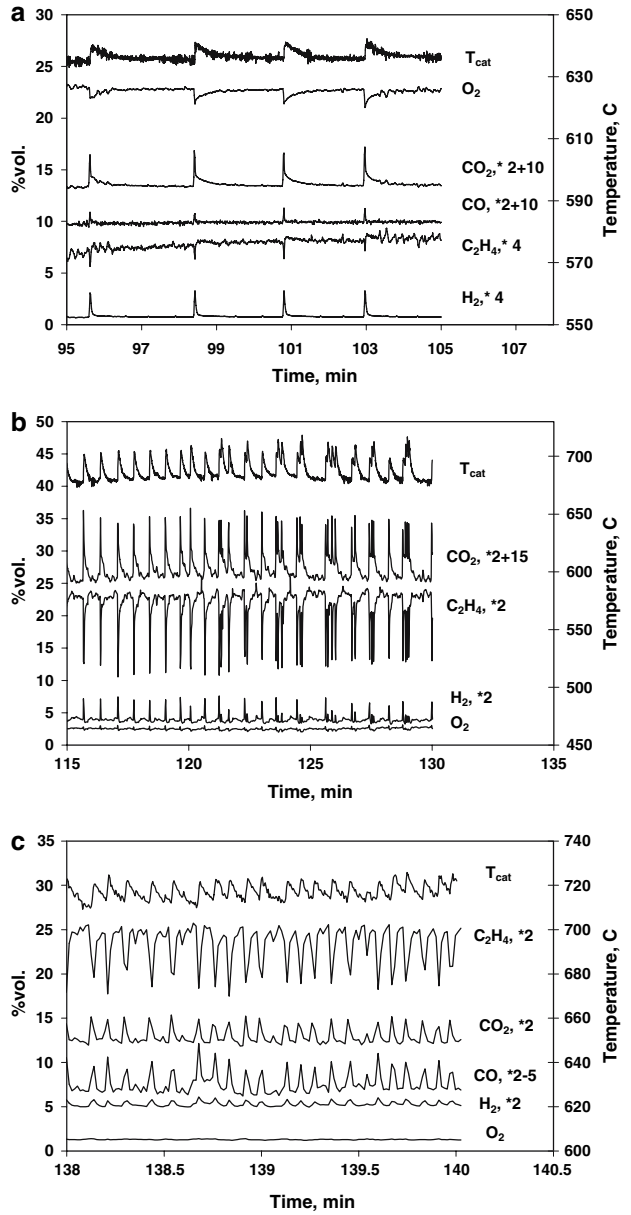

Fig. 1 Effect of reactor temperature on the oscillatory behaviour during ethane oxidation over the Ni foil at flow rate 20 ml/min (C_2H_6 : O_2 : Ar = 17.5:7.5:1): gas phase concentrations and the catalyst temperature, (**a**) T_r = 670 °C, (**b**) T_r = 680 °C and (**c**) T_r = 690 °C

identified as Co_3O_4. The variation of the colour of the pre-reduced Co1 foil during the oxidation at 500 °C is shown in Fig. 2. It can be seen that the initially reduced, metallic sample changes its light colour to black and then to grey after the reactant mixture was introduced into the reactor. Visual observation of the colour changes during the oxidation process can be viewed as movie 1 via the Internet on the homepage of the Institute of Chemical Physics RAS [13] or as supplementary materials associated with this article in the online version of Catalysis Letters.

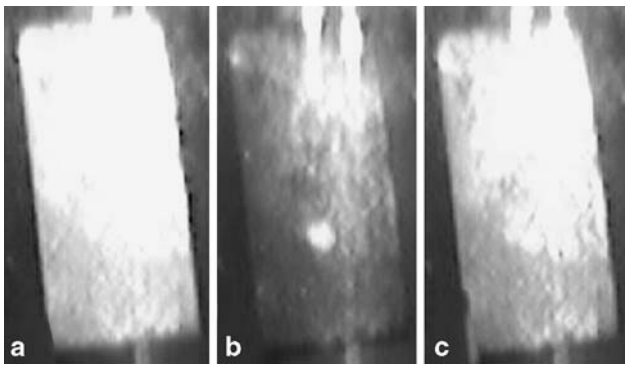

Fig. 2 The variation of the colour of the pre-reduced Co1 foil during the oxidation at 500 °C

Table 3 demonstrates the effect of temperature on oxygen and products concentrations over Co1 catalyst. At T_r = 500 °C a low steady state reactivity with mainly total ethane oxidation was detected. The colour of the surface was grey, indicating the complete oxidation of the catalyst. At T_r = 600 °C the rate of the total oxidation slightly increased together with the CO, H_2 and C_2H_4 production rates. An oscillatory behaviour was detected at T_r = 625 °C, when the rate of partial ethane oxidation significantly increased and the catalyst temperature T_{cat} became higher than T_r. As the reactor temperature was increased up to 650 °C the period of the oscillations decreased and CO, H_2 concentrations became larger than CO_2 concentration. A further increase of the reactor temperature up to 675 °C led to the appearance of the chaotic dynamics on the catalyst surface.

Figure 3 shows a typical example of regular oscillations, which were observed at the flow rate of 40 ml/min over Co1 catalyst. Visual observation of the Co1 foil revealed that periodic variations of the colour of the catalyst occurred simultaneously with the oscillations of the product concentrations. Movie 2 [13] shows the variation of the catalyst surface during the oscillations depicted in Fig. 3. Periodic transitions from the oxidised state (dark colour) to the reduced state (light colour) can be seen. The reduction of the surface began in the downstream part of the catalyst and spread up as a wave across the whole surface. During the movement of the wave corresponding to the surface reduction, spike of CO_2 concentration was detected (point S in Fig. 3). CO and H_2 concentrations reached their maxima later over the completely reduced surface. In contrast to the reduction process, the oxidation of the catalyst began in the upstream part of the catalyst, where the dark spot appeared. With time the black spot spread to the downstream part, covering the whole sample. This process was identified as the formation of partially oxidised cobalt (CoO), which had a very dark colour. Over the oxidised surface CO_2, O_2 concentrations increased, while CO, H_2

Table 3 Effect of temperature (°C) on the dynamic behaviour as well as on the oxygen and products concentrations (%vol.) (C_2H_6 : O_2 : Ar = 17.5:7.5:1, 20 ml/min)

T_r	T_{cat}	O_2	CO_2	H_2	CO	C_2H_4	The dynamic behaviour
500	451	24.3	1.3	0	0	0	Stationary reaction
550	499	24.6	1.5	0	0	0	Stationary reaction
600	563	21.1	4.3	0.15	0.4	0.3	Stationary reaction
625	648	1.0	14	34	30	0.9	Oscillations
	636	7.0	12	1	2	1.7	
650	668	0.5	10	30	30	3	Oscillations
	674	1.1	14	2.5	5	4	
675	697	0.28	12	6	8.5	6.5	Chaotic process

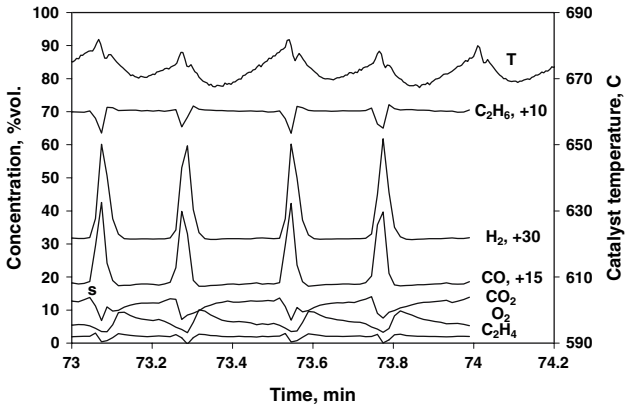

Fig. 3 Regular oscillations during ethane oxidation over Co1 catalyst (C_2H_6 : O_2 : Ar = 17.5:7.5:1, 40 ml/min): gas phase concentrations and the catalyst temperature

concentrations diminished. Figure 3 shows that the waveform of temperature oscillations is rather complicated. It contains large exothermic peaks, which mainly reflect the CO_2 production rate and small endothermic peaks corresponding to CO and H_2 production rates. It can be seen also that the amount of produced ethylene is very small and that the rate of C_2H_4 production reaches its maximum value when the surface is in the oxidised state.

At higher reactor temperatures very complicated dynamic behaviour over the catalyst surface could be detected. Figure 4 demonstrates the sequence of images of the Co2 catalyst surface, which were recorded by the video camera at the reactor temperature of 630 °C. The corresponding movie 3 can be viewed via the Internet [13]. Figure 4a shows that the upstream part of the catalyst is in the steady oxidised state, while some kind of a surface turbulence can be observed in the downstream part of the catalyst surface. Here areas of reduced (light spots) and oxidised surface (dark spots) appear and disappear in a chaotic manner. The upstream and downstream parts of the catalyst are separated by the noticeable static boundary. No macroscopic oscillations of gaseous concentrations were detected under these conditions using the on-line mass-spectrometer. During a gradual increase of the reactor

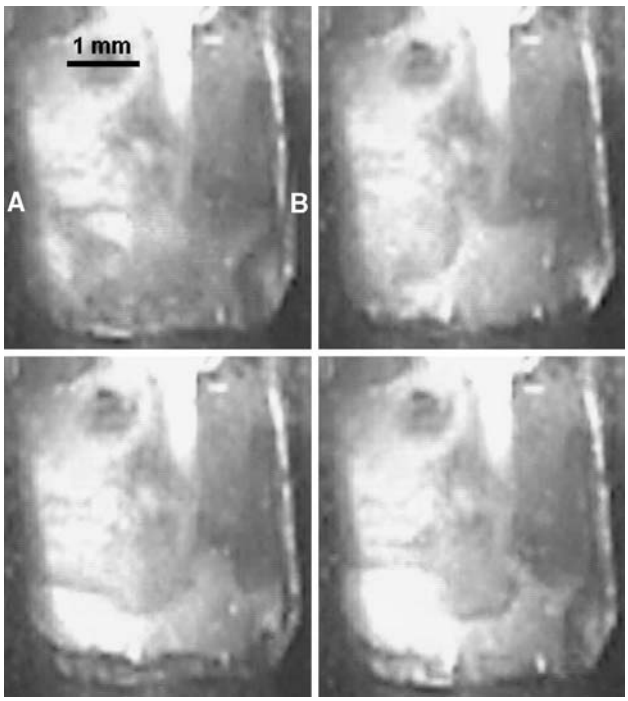

Fig. 4 The sequence of images of the Co2 catalyst surface at T_r = 630 °C (C_2H_6 : O_2 : Ar = 17.5:7.5:1, 20 ml/min)

temperature up to 730 °C the boundary between two parts of the surface shifted to the top of the Co2 catalyst. At 730 °C the upper oxidised part completely disappeared and the surface turbulence was observed over the whole surface. Again macroscopic reaction rate oscillations were not detected. The steady state C_2H_4 concentration was large while the oxygen concentration was close to zero.

To examine additional details of the colour variation during the oscillatory behaviour of Co catalyst particular experiments were carried out over Co1 catalyst with a fresh polished surface. A reaction mixture comprising C_2H_6 : O_2 = 7:3 was supplied at the flow rate of 28 ml/min. Figure 5 shows the sequence of images of the catalyst surface, which were recorded during the oscillatory behaviour. The corresponding movie N4 can be viewed via the Internet [13]. Figure 5a demonstrates the initial reduced

surface of the sample. The propagation of the oxidation front is depicted in Fig. 5b and c. It can be seen that the oxidation wave does not spread through the whole surface and stops with the formation of clear boundary between oxidised (dark) and reduced (light) parts of the surface. Figure 5d–f show the backward motion of the oxidation front. However, the previously oxidised upstream area and downstream reduced part of the catalyst are still separated by the noticeable boundary as can be seen in Fig. 5f. Only after some seconds the dark, newly reduced surface turned the initially light colour. Figure 5g and h demonstrate that several boundary lines can exist after some oscillatory cycles. It can be suggested that the diffusion of oxygen from the oxidised surface into the bulk of the Co foil can occur on the oxidised area of Co sample. The existence of the noticeable boundary after the backward motion of the oxidation front may indicate the situation when the surface is already reduced and not all incorporated bulk oxygen was removed during the time after the reduction started.

4 Discussion

The paper presents information about the first observation of oscillations during ethane oxidation over Ni and Co catalysts. At present, the oscillatory behaviour was discovered during oxidation of all light alkanes over Ni catalysts including methane, ethane and propane and during oxidation of methane and ethane over Co catalysts. All the oscillations demonstrate periodic transitions between two phases of the catalytic process. The first one is characterised by a higher degree of alkane and oxygen conversion and preferential partial oxidation of the alkane to CO and H_2. All experimental data allow to conclude that during this particular oscillatory phase Ni and Co are in the reduced metallic state. Another oscillatory phase is characterised by a lower degree of alkane and oxygen conversion, as well as by a lower degree of partial oxidation with respect to total oxidation and by formation of surface oxides of Ni or Co. The dissociative adsorption of hydrocarbons occurs at a higher activation energy than the dissociative adsorption of oxygen. This may be the reason why in all systems some oscillatory behaviour was detected when the gas phase hydrocarbon/oxygen ratio was very high.

However, there are some differences between oscillatory behaviour during methane and ethane oxidation over nickel catalysts as well as over cobalt catalysts due to a higher reducing ability of ethane then that of methane. The primary difference is that the oscillations during ethane oxidation over both catalysts have higher frequencies in comparison with oscillations during methane oxidation. In the case of the Ni foil the oscillations during ethane oxidation were observed in the same temperature range as the oscillatory behaviour during methane oxidation, but frequencies of the oscillations during ethane oxidation were

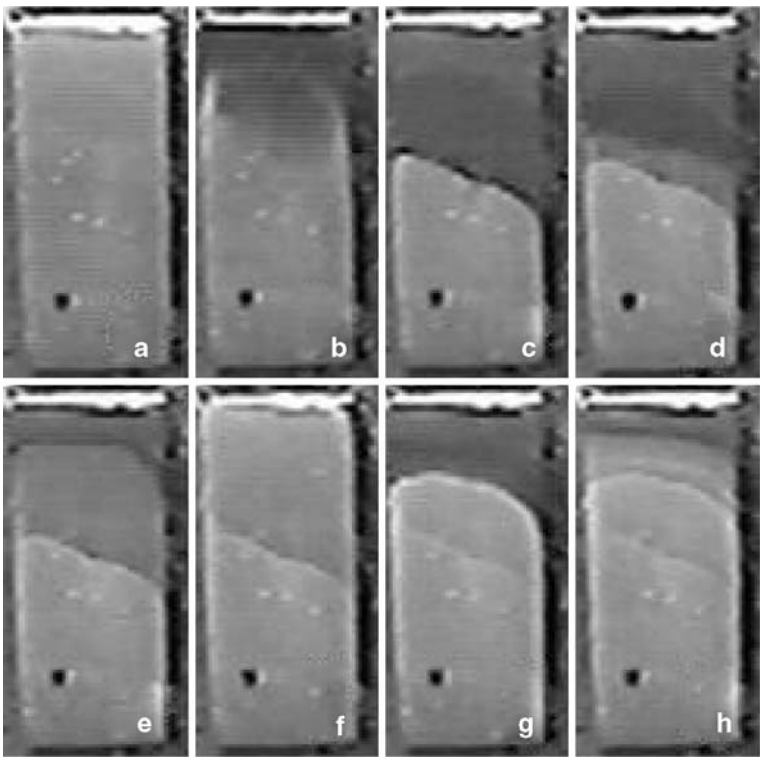

Fig. 5 The sequence of images of the Co1 catalyst surface recorded at the following time points: (**a**) 0.00 s, (**b**) 0.32 s, (**c**) 1.52 s, (**d**) 1.64 s, (**e**) 1.80 s, (**f**) 2.80 s, (**g**) 4.40 s and (**h**) 4.68 s

higher and amplitudes of the oscillations were smaller. In the case of Co foils the oscillatory behaviour during ethane oxidation was detected at temperatures ~300 °C lower than the temperature range of oscillations during methane oxidation. However in spite of lower temperatures frequencies of the oscillations during ethane oxidation were higher than frequencies of the oscillations during methane oxidation.

Mathematical modelling of the oscillatory behaviour during methane oxidation over Ni catalysts showed that the period of the oscillations was defined by the rates of oxidation and reduction processes [10]. The results obtained in this study suggest that this may be the common property of the oscillatory behaviour during hydrocarbon oxidation and higher frequencies of the oscillations during ethane oxidation is the result of a higher reducing ability of ethane.

The application of TGA in combination with on-line mass-spectrometry in our previous studies [6, 8] allowed to identify the distinction in Ni and Co redox properties. It was demonstrated that metallic Co oxidised much more extensively than Ni, and pre-oxidised Co needed much more time for reduction by H_2 or CH_4. These distinctions are responsible for the larger period of the oscillations during methane and ethane oxidation over the Co catalysts in comparison with the period of the oscillations during methane and ethane oxidation over the Ni catalysts.

The other essential difference between Ni and Co catalysts is the existence of various forms of oxidised cobalt. While Ni oxidises only to NiO, two forms of Co oxides exist in the temperature range of our study. Figure 2 demonstrates that oxidation proceeds from metallic Co to CoO and then to Co_3O_4.

Over Co foils the oscillations of methane oxidation were observed at temperatures 750–800 °C, which are higher than the temperature of Co_3O_4 decomposition to CoO, and during the oscillatory behaviour the catalyst surface changed periodically its state between CoO and metallic Co. Oscillations during ethane oxidation over Co foil were detected at temperatures 550–600 °C, under the conditions where Co_3O_4 could exist and could be reduced to CoO due to the higher reducing ability of ethane. Therefore the significant decrease of the temperature range of the oscillations during ethane oxidation over Co in comparison with that of the oscillations during methane oxidation can be explained by the higher reducing ability of ethane. The higher frequencies of oscillations during ethane oxidation can be also connected with the higher reducing ability of ethane in comparison with methane.

The other significant difference between oscillatory behaviour during methane and ethane oxidation is the existence of an additional reaction path, namely the reaction of ethene formation. Our study of ethane oxidation in the empty reactor demonstrated that the gas phase oxidative dehydrogenation of ethane occurred with the low conversion from 525 till 625 °C and with the drastic increase of the reaction rate at 650 °C due to the chain homogeneous reaction. The presence of Ni foil suppress the homogeneous reaction at T_r of 650–670 °C. At higher temperatures the homogeneous ethene formation proceeds along with the heterogeneous oscillations increasing during the low activity, oxidised phase of the oscillations. This may be the result of a higher gas phase oxygen concentration during this period and probably due to a partial heterogeneous oxidative dehydrogenation of ethane that is more preferable over the oxidised surface. In the case of Co foil the oscillations start at temperatures below the range of chain homogeneous ethane oxidation. So ethene evolution during the oscillations over Co catalyst were much lower.

In summary, the oscillations during ethane oxidation over Ni and Co catalysts originate due to the periodic oxidation–reduction of the catalyst surface, the variation of temperature and the selectivity of the process. They have much in common with oscillations during methane oxidation over these catalysts. The primary difference between oscillations during methane and ethane oxidation over Ni and Co catalysts is connected with the higher reducing ability of ethane.

Acknowledgments This work was supported by the Russian Foundation for Basic Researches (RFBR grants 05-03-33128 and 06-03-08196).

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