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A Comparative Study of the Activity of Oxide Catalysts in the Oxidation of Methane and 1,1-Dimethylhydrazine

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Abstract—The catalytic oxidation of methane and 1,1-dimethylhydrazine ($(CH_3)_2N–NH_2$, unsymmetrical dimethylhydrazine (UDMH)) with air on oxide catalysts was studied. Two pairs of perovskites ($Ca_{0.7}Sr_{0.3}FeO_{2.5(3.0)}$ and $La_{0.7}Sr_{0.3}CoO_{2.5(3.0)}$, stoichiometric and superstoichiometric with respect to oxygen) and a supported spinel ($20\%(Cu_xMg_{1-x}Cr_2O_4)/\gamma\text{-}Al_2O_3$, IC-12-73) were used as catalysts. The experiments were performed using two laboratory flow-type systems: in a catalytic fixed-bed reactor (the oxidation of CH_4) and in a gradientless vibrationally fluidized bed reactor (the oxidation of CH_4 and UDMH) at 150–700°C. In the oxidation of CH_4, the IC-12-73 catalyst was more active than the perovskite catalysts, although particular perovskite catalysts can exhibit higher activity in the region of low temperatures. In the oxidation of UDMH, the activity of perovskites in the test temperature region was lower than that of IC-12-73; this correlates with the higher activity of IC-12-73 in the oxidation of CH_4. The $Ca_{0.7}Sr_{0.3}FeO_{3.0}$ and $La_{0.7}Sr_{0.3}CoO_{2.5(3.0)}$ perovskites exhibited similar activities in the deep oxidation of UDMH, which were higher than the activity of $Ca_{0.7}Sr_{0.3}FeO_{2.5}$. A comparison between the selectivities of the conversion of fixed nitrogen, which is a constituent of UDMH, into nitrogen oxides ($S^{N}_{NO_x}$) demonstrated that, on all of the perovskites, S^{N}_{NO} was higher and $S^{N}_{N_2O}$ was lower than the corresponding values on IC-12-73. Additional information on the possible mechanisms of intermediate formation in the adsorption and oxidation of UDMH on IC-12-73 was obtained using Fourier transform IR spectroscopy.

INTRODUCTION

Mixed oxides with a perovskite structure are of considerable interest as efficient heterogeneous catalysts for several types of reactions in environmental catalysis, such as the oxidation of CO and the reduction of nitrogen oxides (NO_x) in automotive exhaust emission control [1, 2] and the oxidation of hydrocarbons and other volatile organic compounds [2], as well as in membrane catalysis and electrocatalytic processes [3]. The oxidation of methane is an important process for both catalytic combustion and other natural gas applications [4, 5]. The development of safe and efficient processes for the neutralization of 1,1-dimethylhydrazine ($(CH_3)_2N–NH_2$, unsymmetrical dimethylhydrazine (UDMH)), which is a hazardous liquid rocket fuel, is one of the most serious environmental problems of current interest. We found [6, 7] that catalytic oxidation is a very promising approach for solving this problem.

Here, we report the results of comparative laboratory studies of the oxidation of CH_4 and UDMH with air on the following oxide catalysts: two pairs of perovskites ($Ca_{0.7}Sr_{0.3}FeO_{2.5(3.0)}$ and $La_{0.7}Sr_{0.3}CoO_{2.5(3.0)}$, stoichiometric and superstoichiometric with respect to oxygen), and a supported spinel ($20\%(Cu_xMg_{1-x}Cr_2O_4)/\gamma\text{-}Al_2O_3$, IC-12-73). The IC-12-73 catalyst was specially designed for the combustion of liquid and gaseous fuels and of organic wastes in fluidized bed reactors that is, catalytic heat generators [8]. This catalyst exhibited the best results in the deep oxidation of UDMH, as compared with a number of other catalysts [6, 7]: it showed a high activity in oxidation to CO_2 and a low selectivity of NO_x formation. In turn, perovskites were chosen because it was of interest to determine the regularities of CH_4 and UDMH oxidation in relation to their catalyst composition. The study was performed in order to compare the activities of catalyst samples in the oxidation of either of the substances and to obtain new data for refining the role of CH_4 as an intermediate in UDMH oxidation in the following mechanism of the given reaction, which was proposed previously [6, 7]:

(1) $(CH_3)_2N{-}NH_2 + [\ ] \longrightarrow [(CH_3)_2N{-}NH_2]_{ads}$;

(2) $[(CH_3)_2N{-}NH_2]_{ads} + [O]_{ads} \longrightarrow [(CH_3)_2N{=}N]_{ads} + [H_2O]_{ads}$;

(3) $[(CH_3)_2N{=}N]_{ads} + [(CH_3)_2N{=}N]_{ads} \longrightarrow [(CH_3)_2N{-}N{=}CH_2]_{ads} + [CH_3N{=}NH]_{ads}$;

(4) $[(CH_3)_2N{-}N{=}CH_2]_{ads} \longrightarrow (CH_3)_2N{-}N{=}CH_2 + [\ ]$;

(5) $[(CH_3)_2N{-}N{=}CH_2]_{ads} + (3 + x)[O]_{ads} \longrightarrow (CH_3)_2NH + CO_2 + [H_2O] + N_2 + NO_x + (3 + x)[\ ]$;

(6) $[CH_3N{=}NH]_{ads} \longrightarrow CH_4 + N_2 + [\ ]$;

(7) $[CH_3N{=}NH]_{ads} + (3 + x)[O]_{ads} \longrightarrow CO_2 + [H_2O] + N_2 + NO_x + (3 + x)[\ ]$,

where [ ] is an active center on the catalyst surface.

EXPERIMENTAL

Preparation of catalysts. The $Ca_{0.7}Sr_{0.3}FeO_{2.5(3.0)}$ and $La_{0.7}Sr_{0.3}CoO_{2.5(3.0)}$ perovskite catalysts were prepared at the Institute of Solid-State Chemistry and Mechanochemistry, Siberian Division, Russian Academy of Sciences with the use of standard solid-phase procedures [3, 9, 10]. The IC-12-73 spinel catalyst was prepared by the incipient wetness impregnation of a spherical γ-Al_2O_3 support with a mixture of Cu and Mg dichromates, followed by thermal decomposition to corresponding chromites at 700°C [6, 11, 12].

Determination of catalytic activity. The activity of catalysts in the oxidation of CH_4 and UDMH was determined using two laboratory flow-type systems: a catalytic fixed-bed reactor and a gradientless vibrationally fluidized bed reactor [13]. The fixed-bed reactor, of vitreous silica, was placed in a tube furnace, and the vibrationally fluidized bed reactor was equipped with a vibrator operating at a frequency of 50 Hz and placed in a furnace with a fluidized bed of silica sand in a flow of air, which provided good heat removal from the reactor and a constant specified temperature. The catalysts were ground, and fractions with a particle size of 0.5–1.0 mm were taken for the experiments. As was found previously (for example, see [14]), these procedures significantly decrease the effect of internal-diffusion inhibition on the heterogeneous catalytic oxidation reactions of organic substances studied under laboratory conditions. The oxidation of CH_4 was performed in fixed-bed reactors [15, 16] and vibrationally fluidized bed reactors at an initial methane concentration $[CH_4]_0 \sim 1.0$ vol % in air, a space velocity $v_0 = 1000$ or 7200 h^{-1}, and $T = 200$–700°C. The oxidation of UDMH was performed in a vibrationally fluidized bed reactor [6, 7] at $[UDMH]_0 \approx 1.2$ vol %, $v_0 = 7200$ or 24000 h^{-1}, and $T = 200$–400°C. To determine the concentrations of the initial substances and oxidation products, an LKhM-8MD gas chromatograph with a thermal-conductivity detector (TCD) was used in the setup with the fixed-bed reactor, whereas a Kristall 2000m gas chromatograph with a TCD and a flame-ionization detector (FID), which operated simultaneously, was used in the setup with the vibrationally fluidized bed reactor. In the latter case, air, CO_2, and N_2O were determined with the TCD, whereas CH_4, dimethylamine (DMA), parent UDMH, formaldehyde dimethylhydrazone (or methylenedimethylhydrazine (MDMH), $(CH_3)_2N{-}N{=}CH_2$)), and other organic intermediates of UDMH oxidation, which occurred in lower concentrations, were determined with the FID [6, 7]. In this setup, the concentrations of CO, NO, and NO_2 were determined with the use of an ECOM SG Plus selective gas analyzer (Austria). In both of these setups, the experiments were performed as follows: the reactor was heated to an initial T; next, a starting reaction mixture was passed through the reactor until steady-state product concentrations were reached in the mixture after the reactor (~20 min), and two or three samples were taken; thereafter, the next reactor temperature was adjusted, etc. In this case, the constancy of the composition of the starting reaction mixture was monitored at regular intervals.

IR spectroscopic studies. Fourier transform IR spectroscopic studies were performed on a BOMEM MB-102 spectrometer (Canada) in order to determine adsorbed UDMH species on the surface of the IC-12-73 catalyst and UDMH oxidation products both on the surface of this catalyst and in a gas phase. Catalyst samples were ground and pressed into rectangular pellets of a size 2 × 1 cm (15–20 mg/cm^2 in thickness). For *in situ* spectroscopic measurements, the pellets were placed in a special high-temperature cell, which allowed us to obtain the spectra of both the pellet and the gas phase in a transmission mode. The samples were pretreated in an atmosphere of oxygen, followed by evacuation at 450°C. The working wavenumber range from 1100 to 4000 cm^{-1} was used; the number of scans per spectrum (repeated IR-beam scanning across the entire range) was 40. The rate of detection was determined with the use of a DTGS germanium detector with a resolution of 4 cm^{-1}. The procedure of UDMH adsorption on the catalyst surface was analogous to that described elsewhere [17]. Otherwise, standard approaches to IR spectroscopic studies of the surface chemistry of solid catalysts were used [18, 19]. The following spectra were measured:

(1) The spectrum of UDMH in a gas phase (a cell at $T = 25$°C).

(2) The spectra of UDMH adsorbed on the catalyst surface at $T = 100$, 200, and 300°C.

(3) The spectra of the products of UDMH oxidation with air at $T = 100$, 200, and 300°C, both on the catalyst surface and in a gas phase.

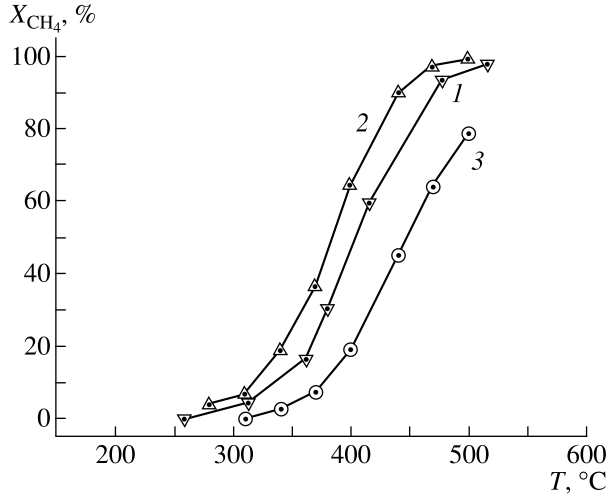

Fig. 1. The temperature dependence of CH_4 conversion in oxidation on the IC-12-73 spinel catalyst in fixed-bed and vibrationally fluidized bed reactors: (*1*) fixed-bed reactor; $v_0 = 1000$ h^{-1}; (*2*) vibrationally fluidized bed reactor; $v_0 =$ 1000 h^{-1}; and (*3*) vibrationally fluidized bed reactor; $v_0 =$ 7200 h^{-1}. $[CH_4]_0 = 0.446$ mmol/l.

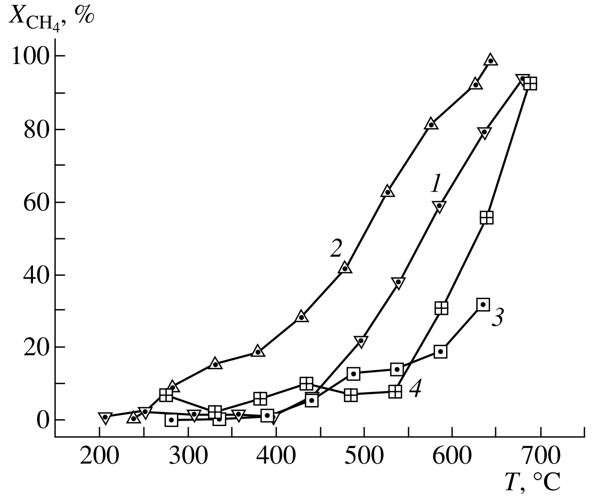

Fig. 2. The temperature dependence of CH_4 conversion in oxidation on $Ca_{0.7}Sr_{0.3}FeO_{2.5(3.0)}$ and $La_{0.7}Sr_{0.3}CoO_{2.5(3.0)}$ catalysts in a fixed-bed reactor: (*1*) $Ca_{0.7}Sr_{0.3}FeO_{2.5}$, (*2*) $Ca_{0.7}Sr_{0.3}FeO_{3.0}$, (*3*) $La_{0.7}Sr_{0.3}CoO_{2.5}$, and (*4*) $La_{0.7}Sr_{0.3}CoO_{3.0}$. $[CH_4]_0 = 0.446$ mmol/l; $v_0 = 1000$ h^{-1}.

RESULTS AND DISCUSSION

Oxidation of CH_4 on the IC-12-73 catalyst. Figure 1 demonstrates the temperature dependence of CH_4 conversion (x) in oxidation on the IC-12-73 catalyst in fixed-bed and vibrationally fluidized bed reactors. It can be seen that, at v_0 = 1000 h^{-1}, X_{CH_4} = 50% was reached at T_{50} = 400°C in the fixed-bed reactor (curve *1*) or at T_{50} = 380°C in the vibrationally fluidized bed reactor (curve *2*); that is, these temperatures are similar. Previously, the oxidation of UDMH in vibrationally fluidized bed and fixed-bed reactors was studied at v_0 = 7200 h^{-1} [6, 7]; therefore, we also studied the oxidation of CH_4 at v_0 = 7200 h^{-1}. As would be expected, an increase in v_0 resulted in an increase in T_{50} up to 450°C (curve *3*).

Oxidation of CH_4 on the perovskite catalysts. Figure 2 demonstrates the temperature dependence of X_{CH_4} in oxidation on the $Ca_{0.7}Sr_{0.3}FeO_{2.5(3.0)}$ and $La_{0.7}Sr_{0.3}CoO_{2.5(3.0)}$ perovskite catalysts in a fixed-bed reactor at v_0 = 1000 h^{-1}. It can be seen that X_{CH_4} = 50% for the $Ca_{0.7}Sr_{0.3}FeO_{2.5(3.0)}$ pair was reached at lower T (570 and 500°C; curves *1* and *2*, respectively) than that for the $La_{0.7}Sr_{0.3}CoO_{2.5(3.0)}$ pair (>635 and 630°C; curves *3* and *4*, respectively). In both pairs, T_{50} in catalysts that are superstoichiometric with respect to oxygen was lower than that in catalysts that are stoichiometric with respect to oxygen.

A comparison of these data with the results on the oxidation of CH_4 on IC-12-73 indicates that the activity of the latter catalyst was higher than that of the perovskite catalysts, although particular perovskite catalysts can exhibit a higher activity at low T, as evident from a comparison between Fig. 1 (curve *1*) and Fig. 2 (curve *2*). High activity at low T due to the anomalously rapid transfer of oxygen ions between microtexture domains in the structure is a characteristic feature of the perovskite catalysts used in this work [3, 9, 10].

Oxidation of UDMH on the IC-12-73 catalyst. Based on previous data on the dependence of the concentrations of the carbon-containing products of UDMH oxidation on $[UDMH]_0$ on the IC-12-73 catalyst in a vibrationally fluidized bed reactor [6, 7], the subsequent experiments with this and other catalysts were performed at $[UDMH]_0$ ~ 0.5–0.6 mol/l and T = 150–400°C in order to cover the regions of partial and deep UDMH oxidation for all of the test catalysts.

Figure 3 demonstrates the temperature dependence of the concentrations of carbon-containing products of UDMH oxidation on the IC-12-73 catalyst. It can be seen that CH_4, DMA, and MDMH intermediate products were present in the region of low T (curves *1, 2*, and *4*). At the same time, the concentration of CO_2 (curve *5*) noticeably increased at $T \geq 220$°C; starting with T = 300°C, carbon from the parent UDMH was almost completely converted into CO_2, along with the formation of CO in an insignificant amount (<0.01 mmol/l). The concentration of unreacted UDMH was no higher than 0.005 mmol/l over the entire temperature range. In experiments on CH_4 oxidation, $[CH_4]_0$ was 0.446 mmol/l, which corresponds to ~50% conversion of the methyl groups of parent UDMH molecules into CH_4 in the oxidation of UDMH.

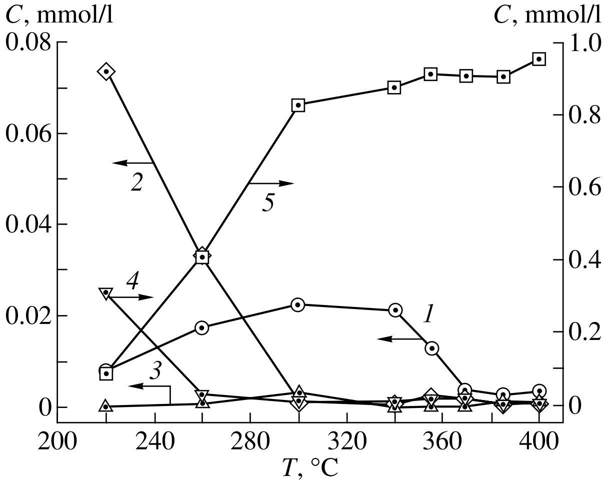

Fig. 3. The temperature dependence of the concentrations of carbon-containing products of UDMH oxidation on the IC-12-73 catalyst in a vibrationally fluidized bed reactor: (*1*) CH_4, (2) DMA, (*3*) UDMH, (*4*) MDMH, and (*5*) CO_2. $[UDMH]_0 = 0.55 \pm 0.05$ mmol/l; $v_0 = 7200$ h^{-1}.

Thus, the results of experiments on CH_4 oxidation can serve as a suitable model for one of the steps of the proposed mechanism of UDMH oxidation [6, 7]. For example, a comparison of Figs. 1 and 3 shows a correlation between the regions of T in which X_{CH_4} noticeably increased and $[CH_4]$ decreased.

In the oxidation of nitrogen-containing compounds, it is of paramount importance to minimize the selectivity of fixed nitrogen conversion into NO_x ($S^{N}_{NO_x}$) [8]. We studied the formation of NO_x in the oxidation of UDMH on the IC-12-73 catalyst and found that the total selectivity was $S^{N}_{NO_x} \leq 10\%$ at 310–400°C (see Table 1). Consequently, the main product of fixed nitrogen conversion under these conditions was N_2.

IR spectroscopic studies. Figures 4 and 5 demonstrate the IR spectra of UDMH adsorption and oxidation products, respectively, on the surface of the IC-12-73 catalyst at various temperatures. Figure 6 demonstrates the spectra of UDMH in a gas phase and of the UDMH oxidation products, which were desorbed into a gas phase, at $T = 200$°C.

The spectra of adsorbed UDMH (Fig. 4) exhibit absorption bands corresponding to a physically adsorbed state (1214, 1306, 1460, and 1588 cm^{-1}). An increase in the temperature of UDMH adsorption ($T \geq 100$°C) shifted an absorption band at 1214 cm^{-1}, which belongs to symmetrical stretching C–N vibrations, to the high-frequency region (1223, 1250 cm^{-1}), as compared with its position in a gas phase [20, 21]. This is likely due to the interaction of an electron pair on the nitrogen atom with the Cr^{3+} transition metal cation, which is a constituent of the catalyst. An increase in the adsorption temperature from 200 to 300°C resulted in the appearance of absorption bands above 2000 cm^{-1}, the highest frequency component of which (2240–2250 cm^{-1}) falls within the stretching vibration region of the C≡N bond [17].

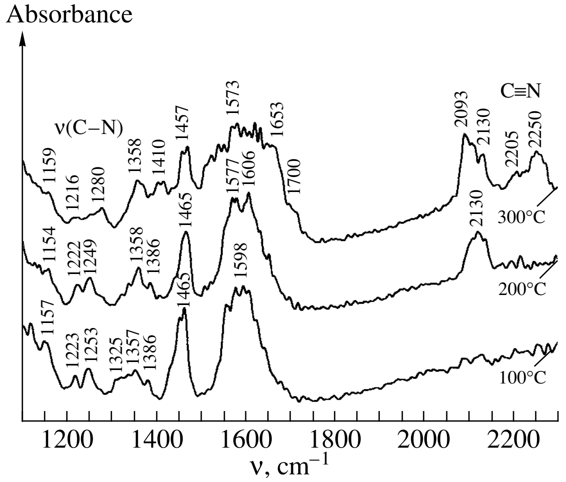

Fig. 4. IR spectra of UDMH adsorption products on the surface of the IC-12-73 catalyst at 100, 200, and 300°C.

An analysis of the spectra of UDMH oxidation products on the catalyst surface (Fig. 5) indicates that, at $T = 100$–200°C, a portion of the intermediate products remained on the surface (absorption bands in the region 1200–1600 cm^{-1}). The spectra at $T = 100$ and 200°C were similar, and Fig. 5 illustrates only the latter case. The interaction of surface compounds formed as a result of UDMH adsorption with oxygen at $T = 300$°C resulted in the almost complete oxidation of UDMH to final products. The spectrum exhibited a broad absorption band at 1630 cm^{-1}, which corresponds to the deformation vibrations of the H_2O molecule adsorbed on the surface [18, 19]. Thus, in the presence of atmospheric

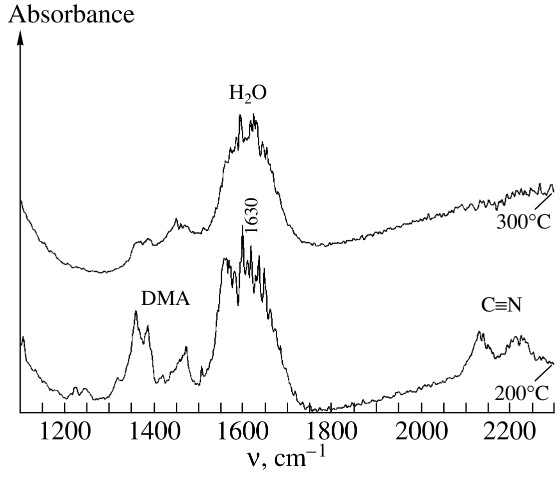

Fig. 5. IR spectra of UDMH oxidation products on the surface of the IC-12-73 catalyst at 200 and 300°C.

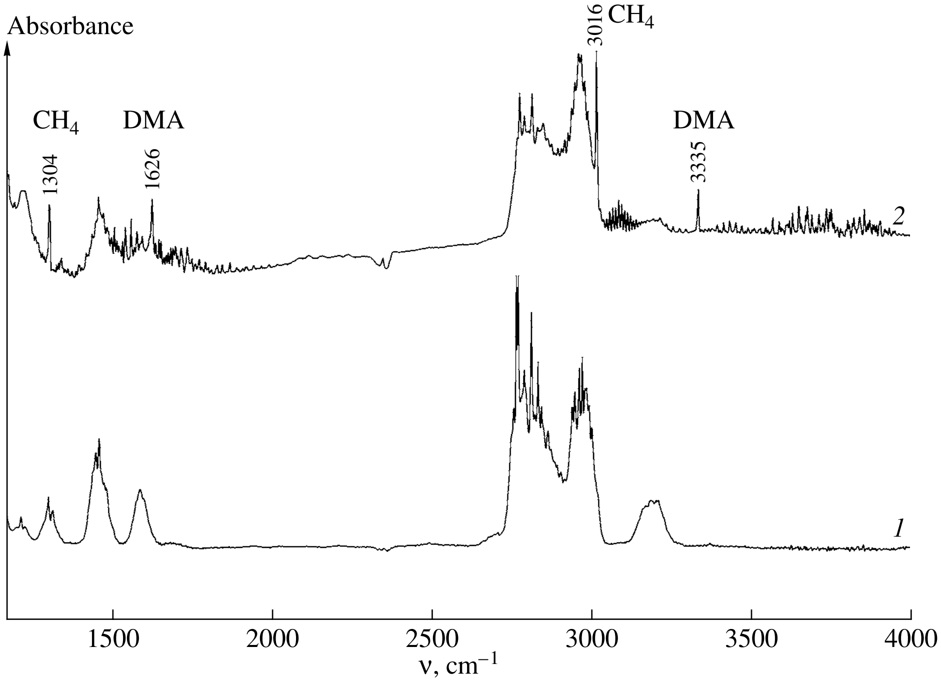

Fig. 6. IR spectra of (*1*) UDMH in a gas phase and (*2*) UDMH oxidation products desorbed into a gas phase on the IC-12-73 catalyst at 200°C.

oxygen as an oxidant, the nature of the interaction of UDMH with the catalyst dramatically changed.

The spectrum of UDMH oxidation products desorbed into a gas phase at 200°C (the spectrum of desorption products at 100°C was identical) (Fig. 6, spectrum *2*) exhibited absorption bands characteristic of the CH_4 molecule (1304, 3016 cm^{-1}) and an intense absorption band at 3335 cm^{-1}, which can be attributed to the stretching vibrations of the N–H bond in the DMA molecule [20, 21]. The intensities of absorption bands due to intermediate products in the spectrum at $T = 300°C$ (not shown) noticeably decreased; at the same time, the intensities of absorption bands in the region 2300–2400 cm^{-1} (low-intensity bands in spectrum *2*) increased; this is indicative of an increase in the formation of CO_2 [18, 19]. These data suggest that, at $T = 100–300°C$, the spectra of UDMH oxidation products correlate well with the spectra of products on the catalyst surface: either intermediates or final products (H_2O on the surface and CO_2 in a gas phase) were observed simultaneously, and this is also consistent with the above data obtained with the use of gas chromatography. Thus, with the use of Fourier transform IR spectroscopy, we have demonstrated that the heterogeneous catalytic oxidation of UDMH is a complex process that results in the formation of a number of intermediate products at low temperatures. This supports the proposed mechanism of this process [6, 7].

Oxidation of UDMH on the perovskite catalysts. Figures 7 and 8 demonstrate the temperature dependence of the concentrations of carbon-containing products of UDMH oxidation on the $Ca_{0.7}Sr_{0.3}FeO_{2.5(3.0)}$ and $La_{0.7}Sr_{0.3}CoO_{2.5(3.0)}$ perovskite catalysts, respectively. On the $Ca_{0.7}Sr_{0.3}FeO_{2.5(3.0)}$ catalysts, starting with the lowest *T*, parent UDMH (curve *3*) was converted into intermediate products, primarily, DMA (curve *2*) and MDMH (curve *4*), and then completely disappeared at $T = 240–280°C$; the noticeable formation of CO_2 began in the above temperature region (curve *5*). In the cases of $Ca_{0.7}Sr_{0.3}FeO_{2.5}$ and $Ca_{0.7}Sr_{0.3}FeO_{3.0}$, the concentrations of CO_2 at 400°C were 0.30 and 0.65 mmol/l, which correspond to 25 and 50% conversion, respectively, in terms of carbon on a $[UDMH]_0$ basis. The $Ca_{0.7}Sr_{0.3}FeO_{3.0}$ and $La_{0.7}Sr_{0.3}CoO_{2.5(3.0)}$ perovskites exhibited close activity levels in the deep oxidation of UDMH, which were higher than the activity of the $Ca_{0.7}Sr_{0.3}FeO_{2.5}$ perovskite (cf. curve *5* in Figs. 7b, 8a, and 8b with curve *5* in Fig. 7a). Note that similar results were obtained in the oxidation of CH_4 and UDMH on perovskites. In both of the reactions, $Ca_{0.7}Sr_{0.3}FeO_{3.0}$ exhibited the highest activity, and a decrease in $[CH_4]$ in UDMH oxidation on $Ca_{0.7}Sr_{0.3}FeO_{2.5(3.0)}$ perovskites occurred at $T \approx 320–400°C$; in this temperature region, the onset of CH_4 oxidation was observed (Fig. 2). In both of the reactions, $Ca_{0.7}Sr_{0.3}FeO_{2.5(3.0)}$ was more active than $La_{0.7}Sr_{0.3}CoO_{2.5(3.0)}$. However, although $Ca_{0.7}Sr_{0.3}FeO_{3.0}$ exhibited the highest activity in CH_4 oxidation, this perovskite exhibited the highest $[CH_4]$ in the oxidation of UDMH. Among the intermediate products, MDMH was predominant on $Ca_{0.7}Sr_{0.3}FeO_{2.5(3.0)}$ ($[MDMH]_{max} \approx 0.40$ mmol/l at $T \approx 250°C$), whereas DMA was predominant on $La_{0.7}Sr_{0.3}CoO_{2.5(3.0)}$

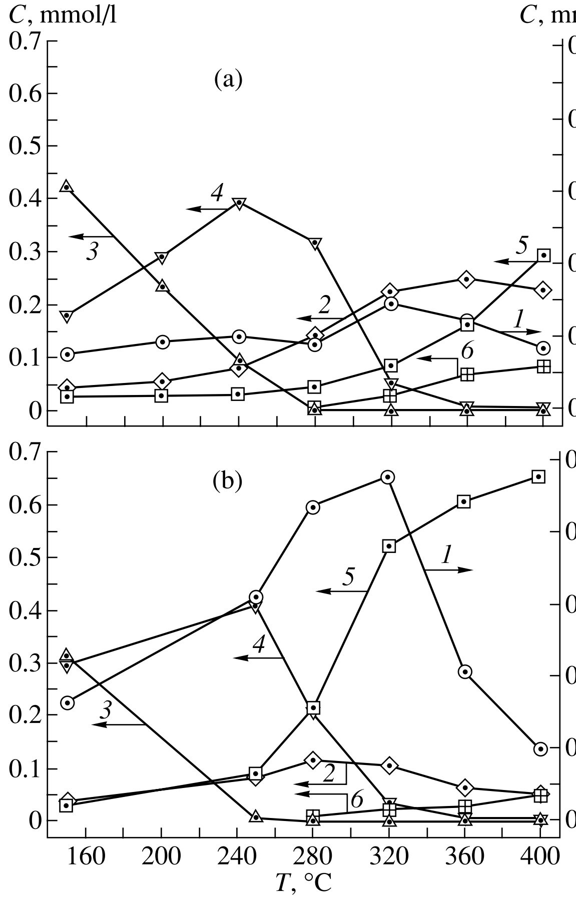

Fig. 7. The temperature dependence of the concentrations of carbon-containing products of UDMH oxidation on (a) $Ca_{0.7}Sr_{0.3}FeO_{2.5}$ and (b) $Ca_{0.7}Sr_{0.3}FeO_{3.0}$ catalysts in a vibrationally fluidized bed reactor: (*1*) CH_4, (*2*) DMA, (*3*) UDMH, (*4*) MDMH, (*5*) CO_2, and (*6*) CO. $[UDMH]_0 = 0.60 \pm 0.05$ mmol/l; $v_0 = 24000$ h^{-1}.

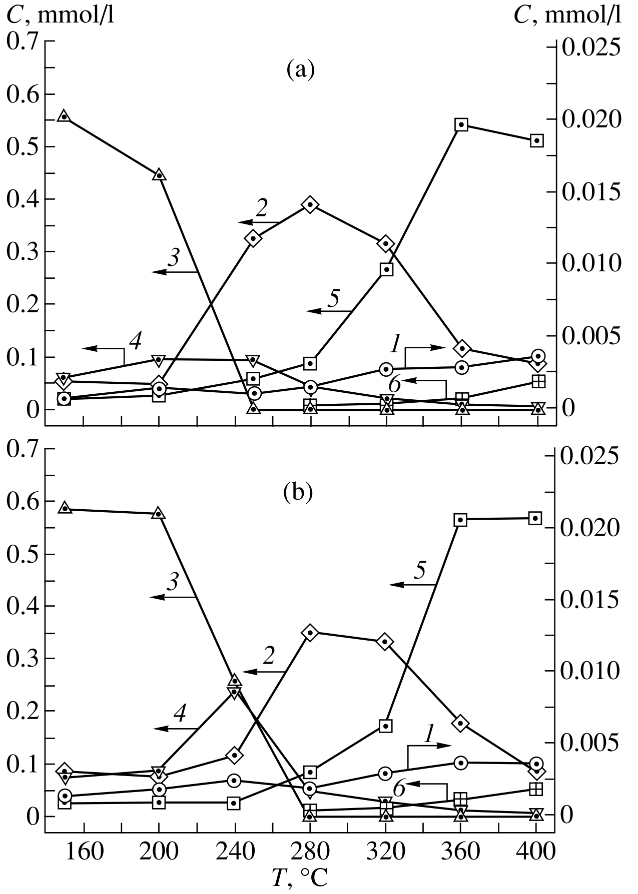

Fig. 8. The temperature dependence of the concentrations of carbon-containing products of UDMH oxidation on (a) $La_{0.7}Sr_{0.3}CoO_{2.5}$ and (b) $La_{0.7}Sr_{0.3}CoO_{3.0}$ catalysts in a vibrationally fluidized bed reactor: (*1*) CH_4, (*2*) DMA, (*3*) UDMH, (*4*) MDMH, (*5*) CO_2, and (*6*) CO. $[UDMH]_0 = 0.60 \pm 0.05$ mmol/l; $v_0 = 24000$ h^{-1}.

($[DMA]_{max} \approx 0.40$ mmol/l at $T = 280$°C). All of the perovskites exhibited similar values of [CO] (curve *6*), which increased with *T*.

Tables 2 and 3 illustrate the temperature dependence of the concentrations and selectivities of N_2O and NO formation from fixed nitrogen in the oxidation of UDMH on the $Ca_{0.7}Sr_{0.3}FeO_{2.5(3.0)}$ and $La_{0.7}Sr_{0.3}CoO_{2.5(3.0)}$ catalysts, respectively. The values of S^N_{NO} were similar for $Ca_{0.7}Sr_{0.3}FeO_{3.0}$ and $La_{0.7}Sr_{0.3}CoO_{2.5(3.0)}$. In the case of $Ca_{0.7}Sr_{0.3}FeO_{2.5}$, lower values of S^N_{NO} were observed, which correlate with the above lower conversion of UDMH into deep oxidation products on this perovskite. The values of $S^N_{N_2O}$ were similar for all of the four perovskites.

A comparison with the results on the oxidation of UDMH on the IC-12-73 catalyst suggests the following:

First, an almost 100% conversion of carbon into CO_2 on IC-12-73 was observed starting at $T = 300$°C, whereas the corresponding value for perovskites was lower than 50% and was reached at higher *T*, of about 360°C. On the other hand, for IC-12-73 at $T > 300$°C,

Table 1. The temperature dependence of the concentrations of N_2O and NO and the selectivities of their formation in the oxidation of UDMH on the IC-12-73 catalyst in a vibrationally fluidized bed reactor

T, °C	$[N_2O]$, ppm	$S^N_{N_2O}$, %	[NO], ppm	S^N_{NO}, %
310	531	4.2	31	0.1
340	650	4.7	31	0.1
370	615	5.1	126	0.5
400	813	6.2	471	1.9

Note: $[UDMH]_0 = 0.55 \pm 0.05$ mmol/l; $\nu_0 = 7200$ h^{-1}.

Table 2. The temperature dependence of the concentrations of N_2O and NO and the selectivities of their formation in the oxidation of UDMH on $Ca_{0.7}Sr_{0.3}FeO_{2.5(3.0)}$ catalysts in a vibrationally fluidized bed reactor

T, °C	$Ca_{0.7}Sr_{0.3}FeO_{2.5}$				$Ca_{0.7}Sr_{0.3}FeO_{3.0}$			
	$[N_2O]$, ppm	$S^N_{N_2O}$, %	[NO], ppm	S^N_{NO}, %	$[N_2O]$, ppm	$S^N_{N_2O}$, %	[NO], ppm	S^N_{NO}, %
280	15	0.1	0	0	0	0	32	0.1
320	48	0.3	64	0.2	0	0	32	0.1
360	60	0.4	223	0.8	43	0.3	446	1.7
400	39	0.3	637	2.3	50	0.4	1146	4.3

Note: $[UDMH]_0 = 0.60 \pm 0.05$ mmol/l; $\nu_0 = 24000$ h^{-1}.

Table 3. The temperature dependence of the concentrations of N_2O and NO and the selectivities of their formation in the oxidation of UDMH on $La_{0.7}Sr_{0.3}CoO_{2.5(3.0)}$ catalysts in a vibrationally fluidized bed reactor

T, °C	$La_{0.7}Sr_{0.3}CoO_{2.5}$				$La_{0.7}Sr_{0.3}CoO_{3.0}$			
	$[N_2O]$, ppm	$S^N_{N_2O}$, %	[NO], ppm	S^N_{NO}, %	$[N_2O]$, ppm	$S^N_{N_2O}$, %	[NO], ppm	S^N_{NO}, %
280	16	0.1	0	0	29	0.2	32	0.1
320	20	0.1	32	0.1	32	0.2	32	0.1
360	23	0.2	446	1.6	29	0.2	191	0.7
400	38	0.3	1114	4.1	72	0.5	1225	4.4

Note: $[UDMH]_0 = 0.60 \pm 0.05$ mmol/l; $\nu_0 = 24000$ h^{-1}.

the concentrations of all the intermediate products were no higher than 0.005 mol/l, whereas these concentrations were higher by one or two orders of magnitude in the case of the perovskites. The difference in the activities of the perovskites and IC-12-73 in UDMH oxidation over the test temperature range correlates with the higher activity of IC-12-73 in CH_4 oxidation, although different experimental conditions should be taken into account for a more accurate determination of this difference: the values of v_0 were 24000 and 7200 h^{-1} for the perovskites and IC-12-73, respectively.

Second, a comparison of the values of $S^N_{NO_x}$ demonstrates that, as a rule, on all of the perovskites S^N_{NO} was higher and $S^N_{N_2O}$ was lower than the corresponding values of IC-12-73. This, along with increased concentrations of UDMH oxidation intermediates formed on the perovskites, suggests that the participation of parent UDMH and intermediate products (such as CH_4 [22]) in the selective catalytic reduction of the formed NO_x on these catalysts is less probable than in the case of IC-12-73. At the same time, the oxidation catalyst activity can decrease due to the strong adsorption of parent UDMH and intermediate products at active sites, as was found previously with the use of other nitrogen-containing compounds as examples [8].

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REFERENCES

1. Tejuca, L.G., Fierro, J.L.G., and Tascon, J.M.D., *Adv. Catal.*, 1989, vol. 36, p. 237.
2. Szabo, V., Bassir, M., Van Neste, A., and Kaliaguine, S., *Appl. Catal., B*, vol. 37, p. 175.
3. Nemudry, A.P., Podyacheva, O.Yu., Ismagilov, Z.R., Ushakov, V.A., and Khairulin, S.R., *Abstr. Russian-Dutch Workshop "Catalysis for Sustainable Development,"* Novosibirsk, 2002, p. 307.
4. Farrauto, R.J. and Heck, R.M., *Catal. Today*, 2000, vol. 55, p. 179.
5. Groppi, G., Ibashi, W., Tronconi, E., and Forzatti, P., *Chem. Eng. J.*, 2001, vol. 82, p. 57.
6. Ismagilov, Z.R., Kerzhentsev, M.A., Ismagilov, I.Z., Sazonov, V.A., Parmon, V.N., Elizarova, G.L., Pestunova, O.P., Shandakov, V.A., Zuev, Yu.L., Eryomin, V.N., Pestereva, N.V., Garin, F., and Veringa, H.J., *Catal. Today*, 2002, vol. 75, p. 277.

7. Ismagilov, Z.R., Kerzhentsev, M.A., Ismagilov, I.Z., Sazonov, V.A., Parmon, V.N., Elizarova, G.L., Pestunova, O.P., Shandakov, V.A., Zuev, Yu.L., Rolin, L.N., Eryomin, V.N., and Pestereva, N.V., *Proc. 32nd Int. Annual Conf. ICT "Energetic Materials. Ignition, Combustion, and Detonation,"* Karlsruhe, 2001, p. 72.
8. Ismagilov, Z.R., Kerzhentsev, M.A., and Susharina, T.L., *Usp. Khim.*, 1990, vol. 59, no. 10, p. 1676.
9. Nemudry, A., Rogatchev, A., Gainutdinov, I., and Schollhorn, R., *J. Solid State Electrochem.*, 2001, vol. 5, p. 450.
10. Nemudry, A., Goldberg, E.L., Aguirre, M., and Alario-Franco, M.A., *Solid State Sci.*, 2002, vol. 4, p. 677.
11. *Promyshlennye katalizatory. Materialy koordinatsionnogo tsentra* (Commercial Catalysts: Data from the Coordination Center), Novosibirsk: Institute of Catalysis, 1990, catalyst IK-12-73, p. 70.
12. Ismagilov, Z.R., Shkrabina, R.A., Barannik, G.B., Dobrynkin, N.M., Sazonov, V.A., Kerzhentsev, M.A., Kirichenko, O.A., and Aleksandrov, V.Yu., *Ross. Khim. Zh.*, 1993, vol. 37, no. 4, p. 48.
13. Shchukin, V.P. and Ven'yaminov, S.A., *Kinet. Katal.,* 1971, vol. 12, p. 533.
14. Ismagilov, Z.R., Dobrynkin, N.M., and Popovskii, V.V., *React. Kinet. Catal. Lett.*, 1979, vol. 10, p. 55.
15. Tsikoza, L.T., Ismagilov, Z.R., Shkrabina, R.A., Koryabkina, N.A., Ushakov, V.A., Kuznetsov, V.V., and Ovsyannikova, I.A., *Sb. trudov seminara pamyati prof. V.V. Popovskogo "Zakonomernosti glubokogo okisleniya veshchestv na tverdykh katalizatorakh"* (Collected Works of the Seminar in Memory of Professor V.V. Popovskii "Deep Oxidation of Substances on Solid Catalysts"), Novosibirsk, 2000, p. 276.
16. RF Patent 2185238, 2001.
17. Evreinov, V.I., Borisova, T.G., Vinogradov, L.M., Emel'yanova, G.I., Lunina, E.V., and Strakhov, B.V., *Zh. Fiz. Khim.*, 1973, vol. 47, no. 2, p. 487.
18. Davydov, A.A., *IK-spektroskopiya v khimii poverkhnosti okislov* (IR Spectroscopy Applied to the Chemistry of Oxide Surfaces), Novosibirsk: Nauka, 1984.
19. Paukshtis, E.A., *Infrakrasnaya spektroskopiya v geterogennom kislotno-osnovnom katalize* (Infrared Spectroscopy in Heterogeneous Acid–Base Catalysis), Novosibirsk: Nauka, 1992.
20. Grekov, A.P. and Veselov, V.Ya., *Fizicheskaya khimiya gidrazina* (Physical Chemistry of Hydrazine), Kiev: Naukova Dumka, 1979.
21. Bol'shakov, G.F., *Khimiya i tekhnologiya komponentov zhidkogo raketnogo topliva* (Chemistry and Technology of Components of Rocket Liquid Propellants), Leningrad: Khimiya, 1983.
22. Shi, C., Cheng, M., Qu, Z., Yang, X., and Bao, X., *Appl. Catal., B*, 2002, vol. 36, p. 173.