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Catalytic Oxidation of Methane by Nitrous Oxide on H[Al]ZSM-5 Zeolite, Silicalite, and Amorphous SiO_2 Modified by Iron, Silver, and Gadolinium Ions

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Abstract—Methane oxidation by an excess of N_2O on the catalytic sites formed in HZSM-5 zeolite, silicalite, and SiO_2 after modification with iron, silver, and gadolinium cations in different combinations is studied. Introduction of iron and silver ions into H[Al]ZSM-5 zeolite is shown to result in the formation of the sites that are active in methane oxidation, while the systems obtained on the basis of crystalline silicalite or amorphous SiO_2 demonstrate poor or no catalytic activity, respectively. Complete oxidation of methane with 100% conversion is observed on the Fe/HZSM-5 and Ag/HZSM-5 catalysts at temperatures higher than 350 and 450°C, respectively. A decrease in the reaction temperature and in the methane conversion is accompanied by coking of the catalysts and, in the case of Fe/HZSM-5, by the appearance of trace amounts of methanol and formic acid in the gas phase. The temperature dependence of the activity and selectivity for the Ag/HZSM-5 and (Ag + Gd)/HZSM-5 catalysts exhibits a pronounced hysteresis at 330–480°C, and the formation of coke proceeds much faster than in the case of iron-containing samples. Catalytic properties of (Fe + Ag)/HZSM-5 are similar to those of Fe/HZSM-5. The introduction of Gd does not influence significantly the activity and selectivity of the catalysts. ESR and TG–DTA were used to determine the state and distribution of Fe, Ag, and Gd in the samples and to examine the processes of coke formation.

INTRODUCTION

The importance of investigations related to the heterogeneous catalytic oxidation of methane is caused by two industrial problems. The first problem is connected with complete oxidation for the removal of traces of hydrocarbons in the processes of the production of extra pure gases. Progress in this field has been achieved due to the use of highly dispersed oxide and zeolite catalysts. The second, even more important problem is related to the production of chemicals by the partial oxidation of cheap and available feedstock, such as natural gas, into oxygen-containing C_1 compounds and products with C–C bonds. However, in spite of numerous research efforts, no cost-effective processes suitable for industrial application [1] have been developed so far.

Experiments with different oxidizing agents (O_2, H_2O_2, NO, N_2O) have shown that the use of nitrous oxide instead of oxygen enables one to increase the selectivity to the partial oxidation products in the process of ethane [2–5] and even methane [6–11] oxidation. Adsorption of N_2O on iron-containing ZSM-5 zeolites leads to the formation of active oxygen species (so-called alpha-oxygen) capable of participating in the oxidation of benzene to phenol [12–14] and methane to methanol [15, 16] at low temperatures. In our previous paper [17], we studied ethane oxidation by N_2O on the zeolites of ZSM-5 type containing iron ions in different localization sites. The temperature dependence of the activity and selectivity with a pronounced hysteresis at 250–350°C was observed for the Fe/HZSM-5 catalyst. The oxidized catalysts that are free from condensation products are active only in the complete oxidation of ethane. The process of oxidative dehydrogenation becomes predominant at low temperatures of the reaction of a $C_2H_6 + N_2O$ mixture with the catalyst, when coke formation takes place and the coordination state of iron is changed [17].

The transformation of methane as the most inert C_1 molecule is a challenging problem. Therefore, the purpose of the present work was the comparative study of the process of methane oxidation by an excess of N_2O on the catalytic sites that are formed after the introduction of iron, silver, and gadolinium ions in different combinations into three types of carriers: (1) H[Al]ZSM-5 zeolite, (2) high-silica silicalite with an ZSM-5 type structure, and (3) amorphous SiO_2 with a large surface area. Gadolinium was used as a paramagnetic analogue of lanthanum, which may influence the acidity of the zeolite and can be detected by ESR [18]. An excess of the oxidizing agent was used to avoid the reduction of iron and silver ions into the metallic state by the reaction mixture, when the aggregation of metal particles could cause the irreversible transformation of the structure of initial catalytic sites formed upon oxidative calcinations of the starting samples.

EXPERIMENTAL

Catalysts

(a) Introduction of iron. Fe/H[Al]ZSM-5. Catalysts containing 0.5 and 1.5 wt % of iron, which were previously studied in ethane oxidation [17], were prepared according to the procedure described in [19] by introducing Fe^{3+} ions into the cationic positions of H[Al]ZSM-5 (Si/Al = 25; PQ Corp.) by incipient wetness impregnation from an aqueous solution of $FeCl_3$. The details of preliminary calcinations of the sample in a vacuum and in air were given in [17].

Fe-Silicalite and Fe/SiO$_2$. Catalysts containing 2 wt % of iron were prepared using the similar procedure [19]. Crystalline silicalite with a ZSM-5 type structure (Si/Al = 280; PQ Corp.) and XRD-amorphous SiO_2 were chosen as carriers. SiO_2 was prepared according to [20, 21], and its specific surface area S_{BET} after calcinations at 540°C for 6 h in an air flow was 680 m^2/g. A specimen of the carrier dried at 60°C was impregnated with an aqueous solution of $FeCl_3$ of a specified concentration. Then, the sample was dried at room temperature in air and calcined in a vacuum (0.1 torr) while ramping the temperature (100°C, 30 min; 200°C, 30 min; 250°C, 30 min; 300°C, 60 min, 400°C, 30 min). No $FeCl_3$ sublimation (m.p. = 296°C) was observed during this treatment. So the entire amount of impregnated iron was retained by the samples. Then the samples were calcined at 520–530°C for 4 h in an air flow.

(b) Introduction of silver and gadolinium. Catalysts containing 0.9–1 wt % of silver or 1.4 wt % of gadolinium were prepared using incipient wetness impregnation of the carriers indicated above from aqueous solutions of silver and gadolinium nitrates, respectively. After drying at room temperature, the samples were calcined in an air flow with a stepwise increase of the temperature (100°C, 30 min; 200°C, 30 min; 300°C, 30 min; 400°C, 30 min; 520°C, 4 h).

(c) Multicomponent systems. The multicomponent systems were prepared by the combination of successive impregnation steps to introduce individual components. The amounts of the introduced components were taken to satisfy the atomic ratio 1 : 1 : 1 (0.5 wt % Fe; 1 wt % Ag; 1.4 wt % Gd) and the total concentration of ions should be ~25% less than the concentration of Brønsted sites in H[Al]ZSM-5 zeolite.

Catalytic Tests

A dry sample (25–100 mg, fraction 0.25–0.5 mm) was placed in a fixed-bed quartz microreactor (~0.2 cm^3) and calcined at 520°C in a dry air flow (50 cm^3/min) for 2 h. Then, the reaction mixture 14.1% N_2O + 1.74% CH_4 + 84.2% He (a twofold excess of the oxidizing agent) was supplied to the reactor (GHSV = 1.6×10^4–2.0×10^4 h^{-1}, atmospheric pressure). In the case of the Fe/SiO_2 and Ag/SiO_2 catalysts characterized by a low activity, the GHSV was 0.8×10^4 h^{-1}. Reaction products were analyzed using a chromatograph equipped with TCD and a Polysorb-1 column.

A series of measurements were performed with a stepwise temperature decrease from 520 to ~260°C. Then, the catalyst was cooled in the reaction mixture, and a series of measurements were taken with a stepwise temperature increase up to 450–520°C. After this experimental cycle, the sample was calcined in an air flow at 750°C for 2 h and then used in the next catalytic cycle.

In some cases, the prolonged (1–2 h) experiments at a constant temperature were performed. In this case, the gas flow at the outlet was switched to the loop trap cooled with liquid nitrogen. Then, the products were analyzed by GC. In one experiment, the products were collected in the trap for 3.5 h and then analyzed by mass spectrometry.

TG–DTA Analysis

Thermal analysis was performed using a MOM Derivatograph-C. The experiments were carried out under static conditions in air with a linear temperature rise (10 K/min) up to 900°C. Similar to the procedure reported in [17], both the initial samples and the coked samples after the catalytic cycle were analyzed. For some of the coked samples, the oxide phase of the catalyst was dissolved in hydrofluoric acid at 20°C and then coke was analyzed by TG–DT.

ESR Measurements[1]

ESR spectra of Fe^{3+}, Gd^{3+}, and coke were measured at –196 and 20°C in X-band (λ = 3.2 cm) using a reflecting Bruker ESP300 spectrometer equipped with a low-temperature 4104 resonator. DPPH was used as the standard. Data processing (base line correction and double integration) was performed using the Bruker ESP300E program kit and WIN-EPR program (version 901201). ESR spectra were measured under conditions of the lack of saturation (UHF power, 6.4 mW) in two different regimes: the spectra of Fe^{3+} and Gd^{3+} ions were registered in the range 100–4100 Oe (two cycles with the sweep time 42 s and a modulation of 4 Oe), and the spectra of coke were registered in the range 3400–3470 Oe (five cycles with the sweep time 10 s and a modulation of 1 Oe).

A fresh catalyst or the sample taken after the catalytic test (25–30 mg) was charged into a quartz ampule with a diameter of 3 mm, calcined in air for 3–5 min, then evacuated and sealed off in a vacuum (~0.01 torr). After the registration of the ESR spectrum of the evacuated sample, air was admitted into the ampule and the ESR spectrum was registered again. After that, in sev-

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[1] ESR measurements were carried out by A.V. Kucherov in the laboratory of Ford Motor Company, Dearborn, USA.

eral cases, the samples were impregnated with distilled water for 1 h, then frozen to –196°C, and ESR spectra were measured.

RESULTS

CH_4 Oxidation with Nitrous Oxide

(a) Fe/H[Al]ZSM-5. The reaction of CH_4 oxidation with N_2O proceeds in a similar way on the Fe/H[Al]ZSM-5 catalysts with the iron contents 0.5 and 1.5 wt % activated at 520 and 750°C. The temperature dependences of the activity (conversion) and selectivity for the 0.5%Fe/HZSM-5 sample are presented in Fig. 1 (curves *1* and *2* correspond to the reaction temperature decrease and curves *1'* and *2'* correspond to the further temperature increase). Complete oxidation of methane with a 100% conversion and 100% selectivity to CO_2 and H_2O is observed at $T >$ 370°C. The activity of the catalyst and selectivity to the products of complete oxidation diminish with a decrease in the temperature (Fig. 1, curve *2*). Coke formation starts under these conditions, and the catalysts become dark gray. It should be emphasized that coking of the catalysts takes place in oxidative conditions (the ratio $N_2O/CH_4 = 8.1$ vs. the stoichiometric ratio equal to 4 corresponding to complete oxidation). When the temperature further increases, the methane conversion turns out to be the same as in the case of the descending temperature profile (Fig. 1), and at $T > 450$°C catalysts become free from coke.

The chromatographic analysis of the reaction products enables one to determine both the amount of CO_2 formed and the consumption of oxidizing agent (N_2O). Therefore, it is possible to calculate the stoichiometry of oxidation (N_2O/CH_4) and to find the temperature dependence of this ratio (Fig. 2). Such a presentation makes it possible to estimate the formal stoichiometry for different stages of methane conversion (reactions (I)–(V)) and to reveal the most interesting temperature region characterized by significant contribution of partial oxidation:

$$CH_4 + 4N_2O = CO_2 + 2H_2O + 4N_2, \qquad (I)$$

$$CH_4 + 3N_2O = CO + 2H_2O + 3N_2, \qquad (II)$$

$$CH_4 + 2N_2O = C + 2H_2O + 2N_2, \qquad (III)$$

$$CH_4 + nN_2O = C_xH_y + nH_2O + nN_2 \text{ (where } n < 2), \qquad (IV)$$

$$CH_4 + nN_2O \longrightarrow \text{oxygenates (where } n = 1, 2 \text{ or } 3). \qquad (V)$$

The difference in the material balance based on the amount of converted methane and the amount of CO_2 formed (Figs. 1, 2), which is attributed to the products of partial oxidation, can be rather high in the region of low CH_4 conversions. However, the procedure used for the analysis of products did not allow us to determine the composition of the reaction products with appropriate accuracy, especially in the case when small amounts of oxygenated products were present in the reaction mixture. Therefore, the technique based on freezing out the products was used to qualitatively estimate the product composition in the case of low conversions of methane. The chromatographic analysis of the products accumulated for 2 h (the catalyst 0.5%Fe/HZSM-5, 300°C) provides evidence for the formation of small amounts of methanol among the reaction products. The mass-spectrometric analysis of the sample accumulated for 3.5 h (catalyst 0.5%Fe/HZSM-5, 300°C) enables us to confirm the presence of CH_3OH and a small amount of formic acid.

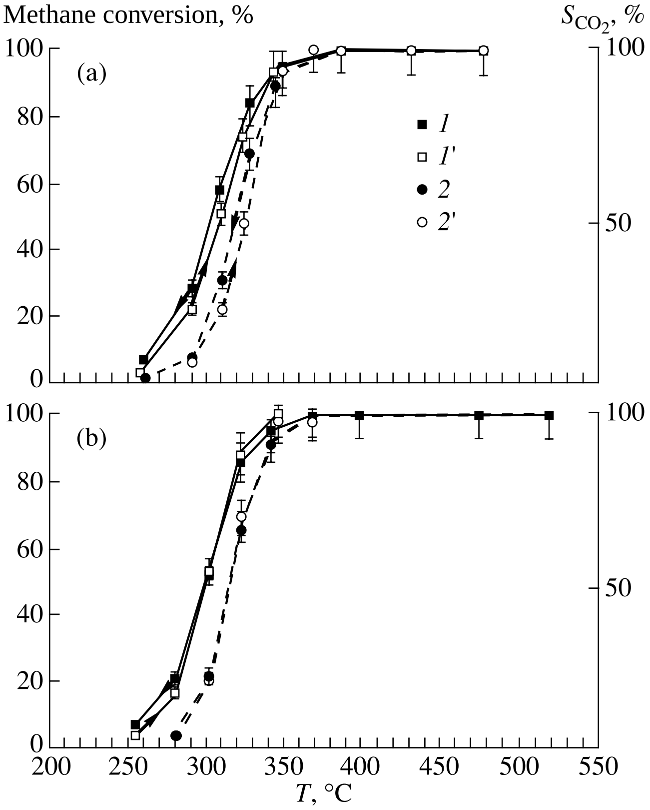

Fig. 1. Dependence of the catalytic activity (*1*, *1'*) and selectivity (S_{CO_2}) (*2*, *2'*) of 0.5%Fe/HZSM-5 calcined at (a) 520 and (b) 750°C on the temperature of methane oxidation by nitrous oxide.

(b) (Fe-Gd)/H[Al]ZSM-5, (Fe–Ag)/H[Al]ZSM-5, and (Fe-Gd-Ag)/H[Al]ZSM-5. The catalytic properties of multicomponent systems prepared by additional modification of 0.5%Fe/HZSM-5 with 1.4 wt % Gd and/or 1 wt % Ag are quite similar to those of the monocomponent Fe/HZSM-5 catalyst. The temperature dependences of the activity and selectivity of the process for the ternary sample (0.5% Fe + 1.4% Gd + 1% Ag)/HZSM-5 are presented in Fig. 3. Multicomponent catalysts become coked and dark-gray in the low-temperature region, and coke is removed at $T > 450$°C just as in the case of the monocomponent Fe/HZSM-5 catalyst.

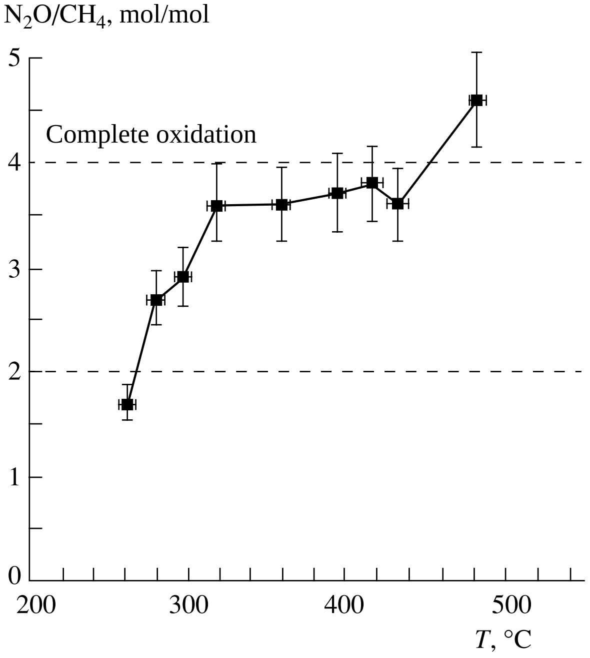

Fig. 2. Dependence of the stoichiometry of methane oxidation (N_2O/CH_4) on the temperature of the reaction.

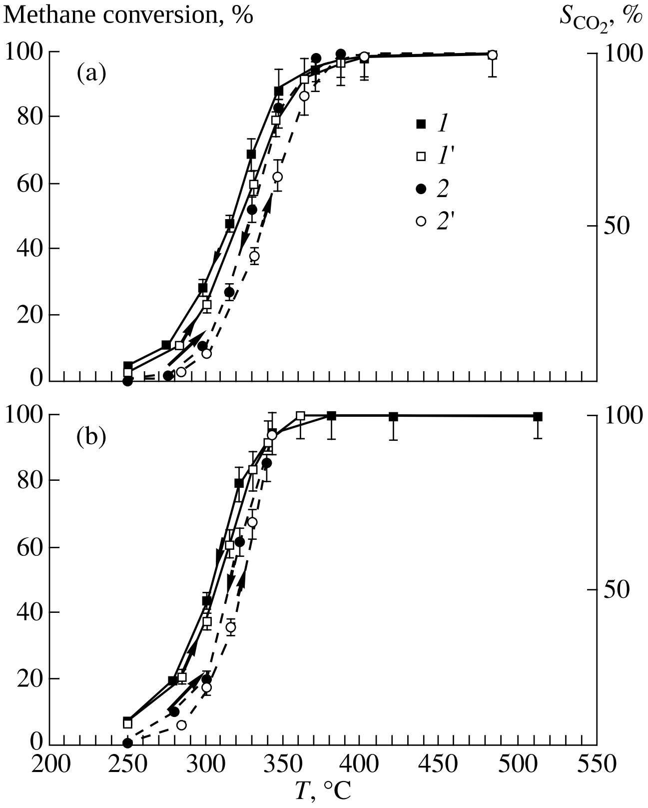

Fig. 3. Dependence of the catalytic activity (*1*, *1'*) and selectivity (*2*, *2'*) of (0.5% Fe + 1.4% Gd + 1% Ag)/HZSM-5 calcined at (a) 520 and (b) 750°C on the temperature of methane oxidation by nitrous oxide.

(c) Ag/H[Al]ZSM-5 and (Gd–Ag)/H[Al]ZSM-5. The oxidation of CH_4 with nitrous oxide on the silver-containing catalysts proceeds at much higher temperatures than in the case of iron-containing samples. The catalysts Ag/H[Al]ZSM-5 and (Gd–Ag)/H[Al]ZSM-5 have similar properties and the process of CH_4 oxidation with nitrous oxide is characterized by a pronounced hysteresis and the appearance of two temperature intervals (Fig. 4). A decrease in the temperature from 520 to ~450°C does not result in any changes: the only reaction gaseous products are the products of complete oxidation. A further decrease in the temperature causes coke formation and a sharp drop in the catalyst activity and selectivity to oxidation products, and the catalysts become black. Upon a further temperature increase, the conversion of methane is much lower than in the case of the descending branch (Fig. 4). The yield of CO_2 increases with increasing temperature (Fig. 4, curve *2*). The analysis of the gas phase at 520–540°C shows that the formation of large amounts of nonstoichiometric CO_2 takes place (the yield of CO_2 reaches 150–170%). This fact indicates the intense burning of coke deposits. Such dependences with a hysteresis presented in Fig. 4 are reproduced after multiple cycles of regeneration and coking of the samples. Calcination of the catalysts at 750°C in an air flow for 2 h does not influence significantly the pattern of the reaction mixture (N_2O + CH_4) transformation. The catalytic properties of the samples still exhibit a pronounced hysteresis shape arising from the coking of the catalyst. The selectivity to CO_2 formation on the coked samples remains virtually unchanged (Fig. 4).

(d) HZSM-5. The oxidation of methane by nitrous oxide on the catalysts with only trace amounts of iron proceeds with a significant rate at much higher temperatures than on other catalysts under study (Fig. 5). The conversion of methane on HZSM-5 at 400°C is lower than 20%, while the conversion on Fe/H[Al]ZSM-5 exceeds 30% already at 300°C. Thus, the reaction rate on the pure HZSM-5 catalyst is considerably lower than on the iron-containing samples. Complete oxidation of CH_4 with a 100% conversion is not observed on HZSM-5 even at 520–530°C (Fig. 5). No hysteresis is observed after the decrease in the reaction temperature to 370°C and a further temperature rise. The contribution of complete oxidation monotonously grows in parallel with the increase in the reaction temperature (Fig. 5).

(e) Iron and Silver-Containing Silicalite and Amorphous SiO_2. The oxidation of CH_4 with nitrous oxide on Fe/silicalite (Fig. 6) proceeds with a significant rate at much lower temperatures than on pure HZSM-5 (Fig. 5), but this system is much less active than Fe/H[Al]ZSM-5 (Fig. 1). Calcination of the catalyst at 750°C for 2 h does not influence significantly the pathways of the reaction mixture (N_2O + CH_4) conversion (Fig. 6b). No pronounced hysteresis is observed in the activity and selectivity of the catalysts.

Ag/silicalite calcined at 520 or 750°C is much less active than Fe/silicalite. To compare these two systems, the conversion of methane on the silver-containing catalyst is given in Fig. 6b (curve *1*').

The catalyst prepared by supporting iron or silver on amorphous SiO_2 has the lowest activity among the catalysts. The temperature dependences of the activity and selectivity for these catalysts measured at a 2.5 times lower space velocity (LHSV = 0.8×10^4 h^{-1}) are presented in Fig. 7. Such conditions were chosen to obtain substantial values of methane conversion on Fe/SiO_2 at 400–550°C. Ag/SiO_2 under such conditions is practically inactive even up to ~530°C (the methane conversion was < 2–3%).

TG–DTA Data

The samples H[Al]ZSM-5, silicalite, and SiO_2 modified by iron (0.5–2 wt %), silver (~1 wt %) as well as two- and three-component systems (Fe–Gd, Fe–Ag, Ag–Gd, and Fe–Gd–Ag) based on these carriers were analyzed before and after the catalytic test. The analyses were performed for the catalysts taken after the catalytic reaction. Some results are summarized in Table 1.

According to the results of DTA, the initial HZSM-5 sample shows no exothermic effects. After the catalytic measurements, the sample is characterized by the exothermic effect (T_{max} ~ 685°C) with a total weight loss of 2.5%; only 0.4 wt % of this amount corresponds to the burning of coke.

As can be seen from Table 1, all the samples are characterized by a stepwise weight loss, and the weight loss observed at a low temperature is connected with water removal. It should be noted that most of DTA curves are not characteristic and have no pronounced exothermic effects connected with the coke burning. The catalyst Ag/H[Al]ZSM-5 is rather uncommon and is characterized by different ratios of weight losses at different stages of DTA before and after the catalytic test. The catalyst 2% Fe/SiO_2 taken after the catalytic test (440°C) exhibits the same weight loss in the high-temperature region (0.9%) as the initial sample. The 2% Fe/silicalite samples show about the same features.

The results obtained for two- and three-component systems are given in Table 2.

It should be pointed out again that DTA curves for the most part of the coked catalysts are not characteristic and have no pronounced exothermic effects in the temperature interval corresponding to the removal of coke. The use of the technique consisting in dissolving the zeolite matrix in HF at 20°C [22] in order to obtain "pure" coke enables one to observe sharp exothermic effects (Table 2, samples 3a-1, 3b-1) and, in several cases, even to identify the type of coke using the value of T_{max} and to speculate about its inhomogeneity.

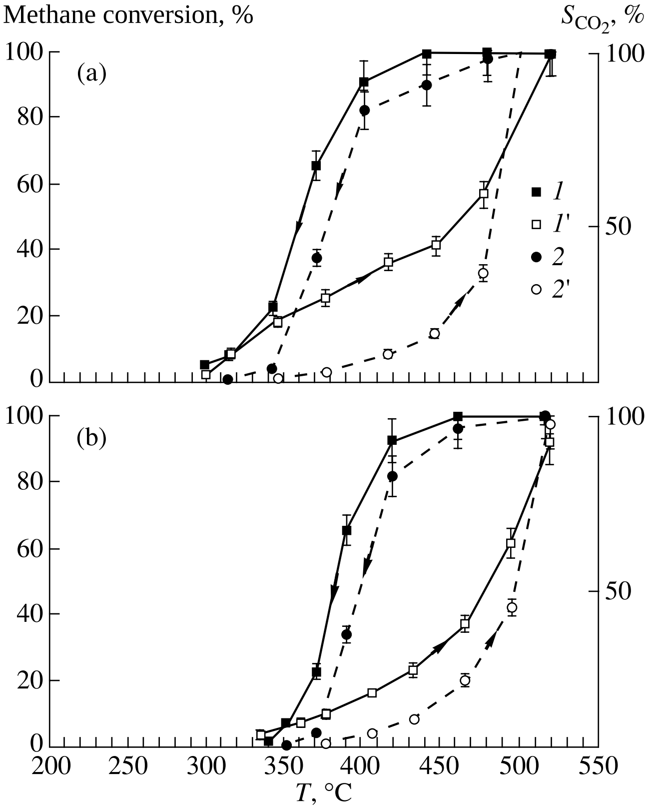

Fig. 4. Dependence of the catalytic activity (*1*, *1*') and selectivity (*2*, *2*') of 0.9%Ag/HZSM-5 calcined at (a) 520 and (b) 750°C on the temperature of methane oxidation by nitrous oxide.

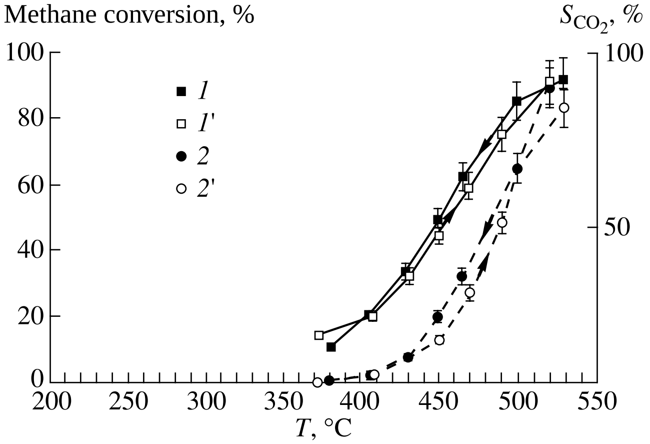

Fig. 5. Dependence of the catalytic activity (*1*, *1*') and selectivity (*2*, *2*') of HZSM-5 calcined at 900°C on the temperature of methane oxidation by nitrous oxide.

ESR Spectra

(a) ESR spectra of paramagnetic ions. The ESR spectra (–196°C) of monocomponent Fe-containing samples based on H[Al]ZSM-5, silicalite, and amor-

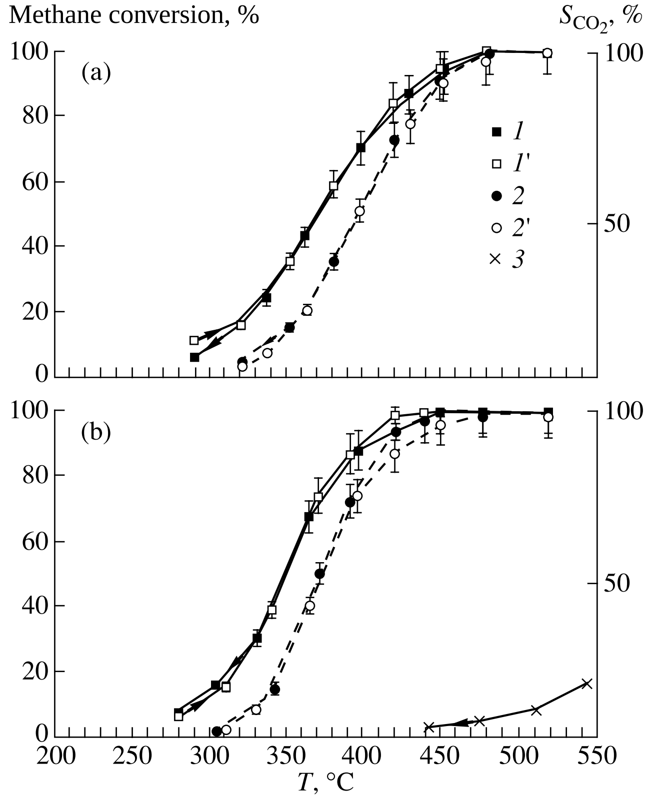

Fig. 6. Dependence of the catalytic activity (*1*, *1*') and selectivity (*2*, *2*') of 2% Fe/silicalite calcined at (a) 520 and (b) 750°C on the temperature of methane oxidation by nitrous oxide; (*3*) conversion on 1% Ag/silicalite.

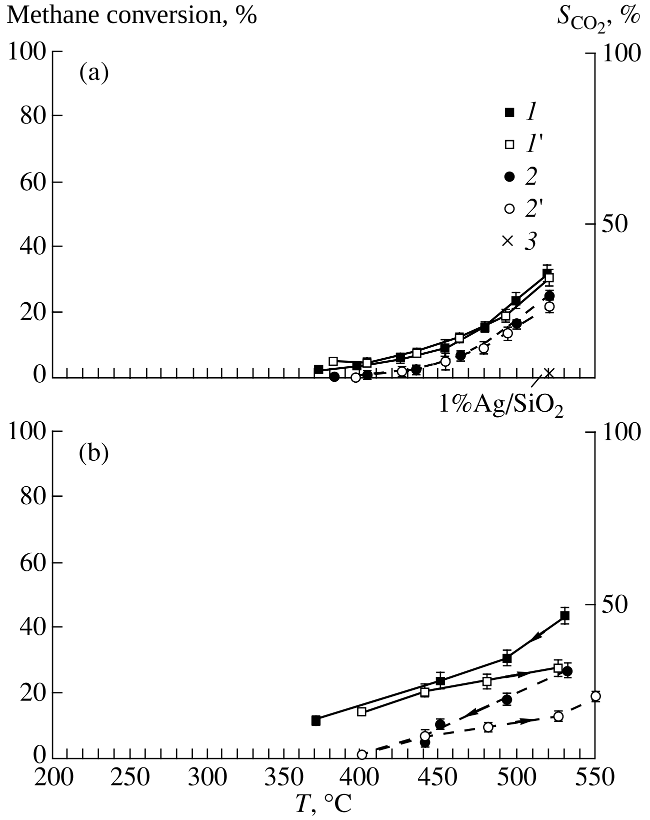

Fig. 7. Dependence of the catalytic activity (*1*, *1*') and selectivity (*2*, *2*') of 2% Fe/SiO$_2$ calcined at (a) 520 and (b) 750°C on the temperature of methane oxidation by nitrous oxide; (*3*) conversion on 1% Ag/SiO$_2$.

phous SiO$_2$ are presented in Fig. 8. The loading was the same. The catalysts were treated in a vacuum before measurements. Calcination at 750°C in air does not change substantially the ESR spectra of iron in H[Al]ZSM-5 (Fig. 8, spectrum *1*). In the case of the catalysts based on silicalite and SiO$_2$, calcination of the samples leads to the formation of a rather broad signal with $g \approx 2.0$ and $\Delta H \approx 2000$ Oe. The ESR spectrum of 1.5% Fe/HZSM-5 is similar to the spectrum presented in Fig. 8 (spectrum *1*).

The ESR spectra (–196°C) of wet monocomponent 1.4% Gd/HZSM-5 and 1.4% Gd/SiO$_2$ samples are shown in Fig. 9. Although the spectra were recorded in different conditions, for the sake of comparison, the ESR spectra (Fig. 10) are recalculated for the same loading and normalized to the same amplification factor.

The ESR spectra of 0.5% Fe/HZSM-5 and (0.5% Fe + 1.4% Gd)/HZSM-5 (20°C, the same loading) calcined at 520°C are given in Fig. 10. Modification of these two samples with 1% Ag does not change the shape of the ESR spectra so that the ESR spectra of (0.5% Fe + 1% Ag)/HZSM-5 and (0.5% Fe + 1.4% Gd + 1% Ag)/HZSM-5 are similar to the ESR spectra *1* and *2* (Fig. 10), respectively. Oxidative treatment of the samples at 750°C does not cause any changes in the spectra presented in Fig. 10.

(b) ESR spectra of coke deposit. The ESR spectra of coked samples after the catalytic test show a narrow symmetrical singlet ($\Delta H \simeq 6$–7.5 Oe, $g = 2.003$) typical of coke. The intensity of the signal of coke in 1% Ag/HZSM-5 is 2–2.5 times higher than that in 0.5% Fe/HZSM-5. The spectra of the catalysts based on SiO$_2$ exhibiting low activity measured after the catalytic tests contains only weak narrow signals of coke. Admitting air into the system leads to a broadening of the narrow signals (by 2–3 Oe), while the integral intensity of the signals decreases ~1.5 times. Regeneration of the samples by calcination in air results in a complete disappearance of the singlet signals from coke.

The ESR spectra of the coked 1%Ag/HZSM-5 sample were registered again after calcination at 850°C in He. After such a treatment, the signal of coke is narrowed by ~1 Oe, and the integral intensities of this signal are substantially different (by 2.2 times) in a vacuum and in air conditions.

Table 1. TG–DTA data obtained for the modified H[Al]ZSM-5 catalysts of methane oxidation by nitrous oxide

No.	Sample	Weight loss, wt % (T, °C)				T_{max}, °C	
		total	1 stage	2 stage	3 stage	DTG	DTA
1	0.5% Fe/H[Al]ZSM-5 calcined at 750°C	7.8	6 (up to 180)	~1.1 (180–520)	~0.7 (>560)	78–80, shoulder at ~180	70–80 (*endothermic*)
1a	0.5% Fe/H[Al]ZSM-5 after the catalytic test	7.1	4.2 (up to 220)	0.5 (220–390)	1.7 (390–590) +0.7 (>900)	74, (390–590)*	~65 (*endothermic*), there is no pronounced exothermic effect
2	1.5% Fe/H[Al]ZSM-5 calcined at 750°C	6.9	4.4 (up to 160)	1.6 (160–620)	0.9 (>620)	75, shoulder at 160	The curve is not characteristic
2a	1.5% Fe/H[Al]ZSM-5 after the catalytic test	3.4	2.1 (up to ~210)	1.3 (~210–900)	–	72	The curve is not characteristic
3a	2% Fe/silicalite after the catalytic test	2.5	1.5 (up to ~200)	1 (~200–900)	–	~70	The curve is not characteristic
4	0.9% Ag/H[Al]ZSM-5 calcined at 750°C	6.1	5.6 (up to 330)	~0.5 (580–900)	–	95	–
4a	0.9% Ag/H[Al]ZSM-5 after the catalytic test	12.3	1.5 (up to ~190)	–	10.3 (425–790)	75, 595	600–605 (*endothermic*) 640 (*exothermic*)
5a	1% Ag/SiO_2, after the catalytic test	1.3	–	~1 (640–900)	–	–	–
6a	0.9% Ag/silicalite, after the catalytic test	2.2	~0.7 (up to ~175)	–	1.4 (~495–690)	~50–60, ~615	~610

* Broad area of weight loss without a pronounced maximum.

DISCUSSION

Catalytic Oxidation of Methane by Nitrous Oxide on Iron-containing Samples

Catalytic oxidation of CH_4 by an excess of N_2O on Fe/H[Al]ZSM-5 proceeds with a sufficient rate at $T >$ 250°C, and the catalysts with different iron contents (0.5 and 1.5 wt % Fe) and calcined at different temperatures (520 and 750°C) have practically similar properties (Fig. 1). Only the complete oxidation of methane into CO_2 and H_2O is observed at $T > 320$°C (Fig. 2), and at $T > 370$°C the conversion of methane achieves 100%. At temperatures below 350°C, the activity of the catalyst and the selectivity to the products of complete oxidation decrease (Fig. 1, curve *2*; Fig. 2) in parallel with the catalyst coking. The catalytic properties of multicomponent samples, which contain 1.4% Gd and/or 1% Ag except for iron (Fig. 3) are identical to the properties of the monocomponent Fe/HZSM-5 system (Fig. 1). Two different reaction pathways can be distinguished:

(1) High-temperature complete oxidation of methane. The complete oxidation of methane by nitrous oxide on iron-containing samples prepared on the basis of H[Al]ZSM-5 and calcined at 520–750°C in air proceeds with 100% conversion and selectivity at $T > 370$°C and does not depend on the temperature and time on stream. Only CO_2 and H_2O can be observed at the reactor outlet. No substantial deterioration of the activity of the catalyst was noticed at $T > 420$°C even in long-run tests. It was shown in our previous studies [17] that the catalytic oxidation of ethane by an excess of N_2O on Fe/HZSM-5 proceeds in a similar way at temperatures higher than 380°C. Thus, the system Fe/HZSM-5 appears to be quite active even in the complete oxidation of methane, the least active molecule among alkanes, by nitrous oxide. This result, however, could have only a limited practical interest, because these catalysts could be used only in the process of simultaneous elimination of N_2O and CH_4 as greenhouse gases [23] or the complete combustion of nitrogen oxides in engines that use natural gas as a fuel.

Table 2. Comparison of multicomponent catalysts based on H[Al]ZSM-5 according to TG–DTA

No.	Sample	Weight loss, wt % (T, °C)				T_{max}, °C on the DTG curve	T_{max}, °C on the DTA curve
		total	1 stage	2 stage	3 stage		
1a	Fe–Ag/H[Al]ZSM-5 calcined at 520°C, after the catalytic test	8.0	5.2 (up to 315)	–	2.3 (315–615)	85, 515	~65, ~400
1b	Fe–Ag/H[Al]ZSM-5 calcined at 750°C, after the catalytic test	4.8	3.0 (up to 230)	~0.6 (230–415)	~1.0 (415–615)	~75, 508–510	The curve is not characteristic
2a	Fe–Gd/H[Al]ZSM-5, calcined at 520°C, after the catalytic test	9.3	2.2 (up to ~185)	0.45 (185–320)	6.2 (320–600)	~90, 495	65–70, 345–480
2b	Fe–Gd/H[Al]ZSM-5, calcined at 750°C, after the catalytic test	7.0	3.8 (up to ~240)	0.9 (~240–~390)	1.9 (~390–615)	76–78, 340, ~500	There are no pronounced effects
3a	Ag–Gd/H[Al]ZSM-5, calcined at 520°C, after the catalytic test	14.0	2.5 (up to 215)	–	10.8 (~345–~710)	~70, 583–584	445 (endothermic), there is no pronounced exothermic effect
3b	Ag–Gd/H[Al]ZSM-5, calcined at 750°C, after the catalytic test	11.3	~3 (up to 295)	–	7.8 (~295–~720)	70, 594	~55, at ~320–370
3a-1	Ag–Gd/H[Al]ZSM-5, calcined at 520°C, after the catalytic test and treatment with HF	95.0	20.9 (up to ~310)	–	68.8 (~310–645)	~70, 2nd maximum is unclear, 520°C	510–512 (*exothermic*)
3b-1	Ag–Gd/H[Al]ZSM-5, calcined at 750°C, after the catalytic test and treatment with HF	86.7	10.4 (up to ~125)	27.5 (~125–360)	43.3 (360–~590)	60, 198, shoulder at 230, the peak with two maxima at 485 and 500	485–490 (*exothermic*)
4a	(Fe–Ag–Gd)/H[Al]ZSM-5, calcined at 520°C, after the catalytic test	7.4	4.6 (up to ~245)	0.5 (~245–335)	1.5 (335–590)	73–75, 450	~65, there is no pronounced exothermic effect
4b	(Fe–Ag–Gd)/H[Al]ZSM-5, calcined at 750°C, after the catalytic test	6.1	–	4.7 (up to 265)	1.1 (265–595)	75–78, (265–595)*	~60

* Broad area of weight loss without a pronounced maximum.

(2) Low-temperature reaction between CH_4 and N_2O on Fe/HZSM-5. The low-temperature reaction (250–330°C) on Fe/HZSM-5 catalysts demonstrates some peculiarities. First, the process of complete oxidation is suppressed. Second, trace amounts of the products of partial oxidation such as methanol and formic acid can be detected in the gas phase. Third, the process of condensation (coking) becomes dominant in spite of oxidative conditions (a twofold excess of N_2O), and significant coking of the catalysts is observed.

In this case, the properties of the samples have a lot in common with those observed in ethane oxidation with an excess of N_2O on Fe/HZSM-5 [17]. Nevertheless, in the case of more reactive C_2H_6 molecules, all the reactions proceed more intensively, resulting in the formation of larger amounts of coke, which is responsible for the appearance of the hysteresis in the temperature dependence of the activity and selectivity of the catalysts. The state of iron in the catalysts undergoes irreversible changes in the process of ethane oxidation [17]. In the case of CH_4 transformations, coke forma-

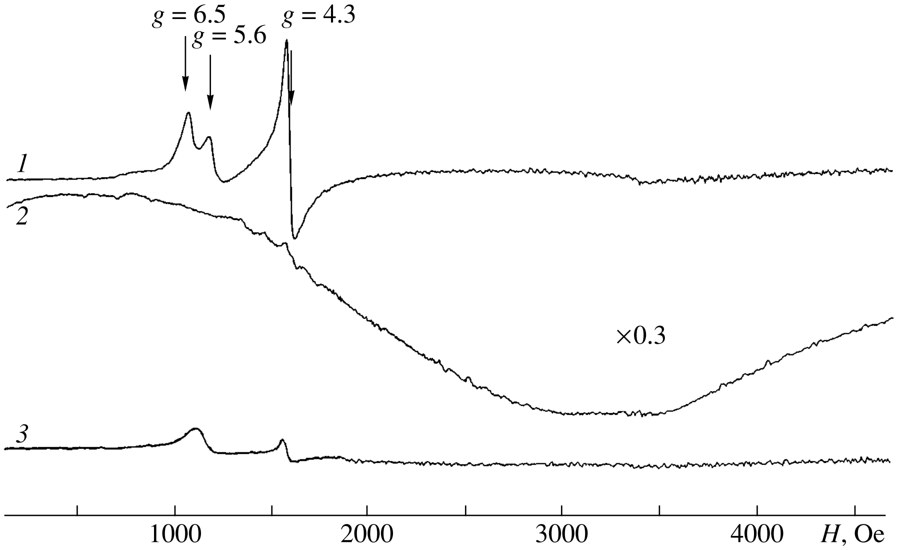

Fig. 8. ESR spectra (–196°C) of (a) 0.5% Fe/HZSM-5, (b) 2% Fe/silicalite, and (c) 2% Fe/SiO_2 calcined at 520°C and then evacuated at room temperature.

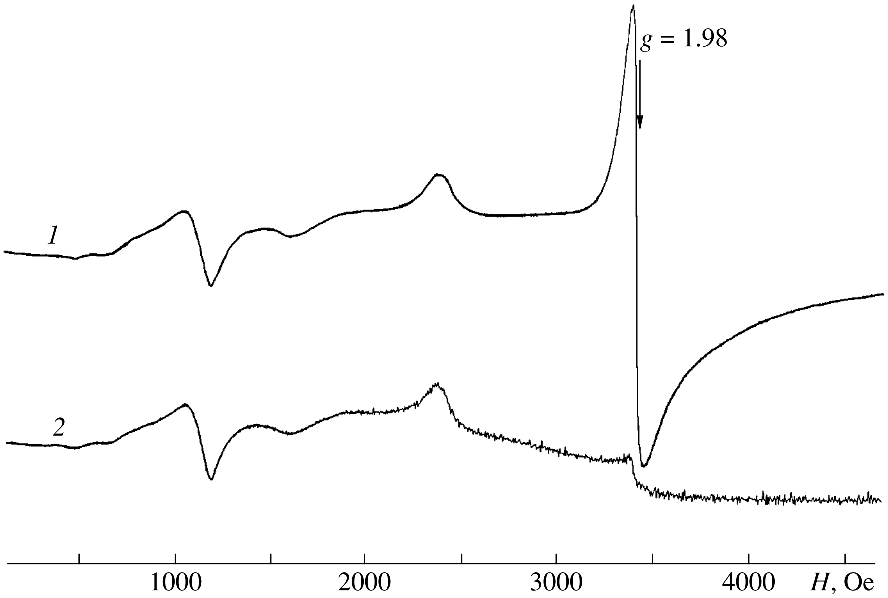

Fig. 9. Normalized ESR spectra (–196°C) of (a) 1.4% Gd/HZSM-5 and (b) 1.4% Gd/SiO_2 calcined at 520°C and then impregnated with water.

tion proceeds with a lower rate; that is why no pronounced hysteresis is observed when comparing the ascending and descending branches of the temperature dependence of the methane conversion (Fig. 1).

It should be noted that, in the region of low-temperature partial oxidation of methane, the process of coke formation becomes predominant, whereas such valuable oxygen-containing products as methanol and formic acid are formed in the gas phase only in trace amounts. It is quite clear that the process of methane conversion into condensation products has no practical interest. This result demonstrates the difficulties that arise in the process of catalytic synthesis of oxygen-containing compounds from methane with reasonably high yields using a continuous catalytic process [1]. The major explanation of these difficulties is the higher reactivity of the oxygen-containing compounds that are believed to be formed compared with methane; therefore, these unstable products are further converted into CO_2 and H_2O or coke in the reaction conditions. Panov with coworkers argued [15, 16, 24, 25] that it is possible to prepare CH_3OH in 100% yield at low temperatures

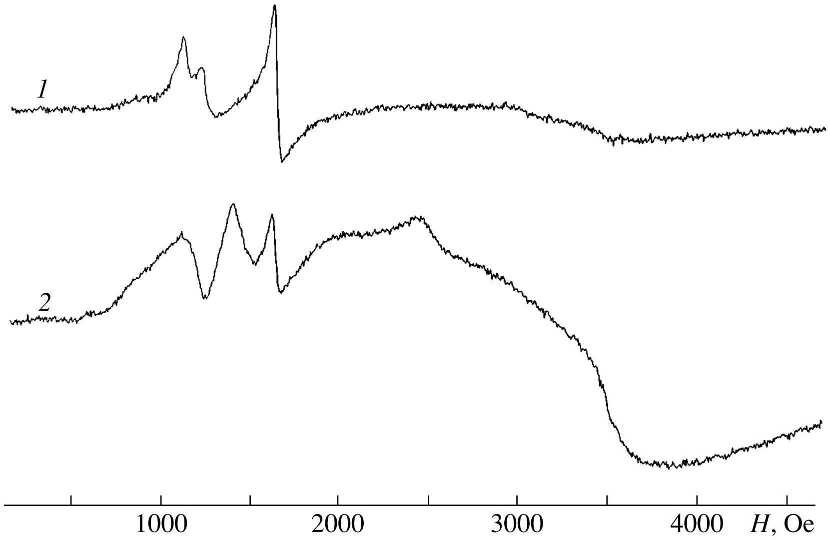

Fig. 10. ESR spectra (20°C) of (*1*) 0.5% Fe/HZSM-5 and (*2*) (0.5% Fe + 1.4% Gd)/HZSM-5 calcined at 520°C and then evacuated at room temperature.

using the successive reaction of Fe/HZSM-5 with N_2O and then with CH_4. However, in this case, methanol molecules are strongly held by the active sites and can be removed only by extraction. An increase in the temperature leads to the secondary reactions of CH_3OH with the formation of CO and CO_2. Therefore, some uncommon methods (such as nonisothermic and (or) cyclic processes) should be used to obtain oxygen-containing C_1 molecules as the main reaction products.

Influence of Gd and (or) Ag on the Properties of Fe/H[Al]ZSM-5

Silver and gadolinium ions were chosen as potentially interesting doping agents (atomic ratio 1 : 1 : 1) for the modification of Fe/H[Al]ZSM-5. Silver was chosen in view of its well-known oxidative properties, and the introduction of silver could change the redox properties of the system. Gadolinium, which is a paramagnetic analogue of lanthanum, can influence the acid–base properties of the zeolite support and, thus, suppress the formation of condensation products.

However, as was already mentioned, the catalytic properties of multicomponent samples containing Gd and/or Ag are quite similar to the properties of the monocomponent 0.5% Fe/HZSM-5 system (Figs. 1, 3).

In fact, the stabilization of silver ions in H[Al]ZSM-5 does lead to the formation of new catalytic sites active in the oxidation of methane (Fig. 4), but this monocomponent system has a considerably lower activity as compared with Fe/H[Al]ZSM-5 and the catalyst deactivation as a result of coking is much faster (Fig. 4). The Ag/H[Al]ZSM-5 samples will be discussed in detail later. It should be noted that less active Ag-containing sites in the binary Ag + Fe system do not contribute substantially to the reaction of methane oxidation as compared with much more active Fe-containing sites. The only difference in the properties of the binary Fe + Gd system is the higher deactivation rate (Tables 1, 2). The effect of the presence of lanthanide ions is not observed in the ternary Fe + Gd + Ag system (Table 2).

It follows from Table 2 that calcination of the catalysts at a high temperature (750°C) causes a gradual suppression of coking of the catalysts as compared with the same samples calcined at 520°C. Therefore, significant suppression of the process of the coke formation can be related with high-temperature dehydroxylation of the zeolite.

Interaction between CH_4 and N_2O on HZSM-5

The activity of pure HZSM-5 containing ~0.03 wt % Fe in the reaction of methane oxidation is considerably lower than the activity of iron-containing samples (Fig. 5). Some activity of the initial zeolite can be caused by either iron traces [26] or the presence of defect redox [27] or Lewis [28] sites. However, the higher catalytic activity of ~0.5% Fe/HZSM-5 can be explained exclusively by the formation of iron species that are active in the oxidation of methane. The introduction of additional amounts of iron oxide does not change the catalytic activity and selectivity of the process.

Peculiarities of the Reaction of CH_4 with N_2O on Iron Oxide Supported on Silicalite and Amorphous SiO_2

The concept of the specific stabilization of iron ions in H[Al]ZSM-5 zeolite in the form of specific binuclear complexes [12, 29–31] or coordinatively unsaturated isolated cations [19, 32, 33] is being actively discussed in the literature. That is why one of the main goals of this work was to compare the activities of iron-containing catalysts supported on a matrix that differs from H[Al]ZSM-5, such as silicalite (crystalline ZSM-5 with admixtures of framework Al) and amorphous SiO_2 with a high surface area.

As can be seen from Fig. 6, the catalyst 2% Fe/silicalite shows a reasonably high activity in the oxidation of methane, but the temperatures necessary for reaching the same conversion are 50–60°C higher than on 0.5% Fe/H[Al]ZSM-5 (Fig. 1). Extrapolation to the region of low conversions provides evidence that the reaction rates for these two catalysts at the same temperature and low conversions of methane differ eight to ten times. It should be mentioned that the silicalite used in this work was not a pure silica and contained some amount of framework aluminum (Si/Al = 280), which is approximately ten times lower than in the case of H[Al]ZSM-5 (Si/Al = 25). Thus, the activity of the sample based on silicalite can be explained by the presence of admixed sites typical of Fe/H[Al]ZSM-5. If the statistic distribution of admixed Al in the framework of silicalite is assumed, then the results obtained fit better to the concept of isolated monocationic sites rather than to the idea of binuclear Fe–O–Fe sites.

The catalytic activity of the supported Fe/SiO_2 system at temperatures below 450°C is negligible (Fig. 7). The comparison of the extrapolated results normalized for the same contact time indicates that the specific activity of Fe/SiO_2 is three to four orders of magnitude lower than that of the Fe/H[Al]ZSM-5 system. So amorphous silica gel with the specific surface area 680 m^2/g, i.e., surface areas typical of zeolites, is not capable of stabilizing active Fe sites similar to those formed in the channels of the H[Al]ZSM-5 zeolite in terms of the oxidation activity.

Interaction of CH_4 with N_2O on Silver-Containing Catalysts

As was shown in this study, the stabilization of silver ions in H[Al]ZSM-5 leads to the appearance of catalytic activity in the process of methane oxidation (Fig. 4). But the Ag/H[Al]ZSM-5 system is considerably less active than Fe/H[Al]ZSM-5 (Figs. 1, 4) and is deactivated by coke formation very rapidly. The temperature dependence of the Ag/HZSM-5 activity and selectivity in the process of methane oxidation by an excess of N_2O at 350–520°C exhibits a pronounced hysteresis. The oxidized catalysts free from condensation products are active only in the complete oxidation of methane. At reaction temperatures below 430°C, the process of complete oxidation is essentially suppressed and the process of coke formation predominates. The catalysts became black, and the amount of coke in the catalysts reaches 10–12 wt % (Table 1). The modification of the Ag-containing H[Al]ZSM-5 catalyst with 1.4 wt % of Gd virtually does not change its catalytic properties (Table 2). The main reaction in the partial oxidation of CH_4 on the Ag/H[Al]ZSM-5 catalyst is the formation of condensation products (coke). Moreover, this process is more intense than in the case of Fe/H[Al]ZSM-5.

The activity of the supported Ag/silicalite system is very low (Fig. 6b). In the case of Ag/SiO_2, no significant CH_4 conversion is observed up to 520°C even at low LHSV. Thus, the introduction of silver in H[Al]ZSM-5 also leads to the specific stabilization of active oxidation species, while amorphous silica gel cannot provide such stabilization.

Nature of Coke

The results of DTA and ESR are in good agreement with each other and allow us to shed some light on the nature of carbon deposits on the samples. The narrow ESR signal of coke for all samples is almost insensitive to the presence of oxygen, which is typical of amorphous and slightly graphitized carbon deposits. Coke of similar nature but in larger amounts is formed in the process of ethane oxidation [17]. Calcination of the coked catalysts in a He atmosphere significantly changes the ESR signal of coke, which indicates the graphitization of amorphous coke deposits. The amount of coke accumulated during the catalytic reaction on the Ag/H[Al]ZSM-5 system is 2–2.5 times larger than on the Fe/H[Al]ZSM-5 system for the same period of time. The burning of this coke proceeds at considerably higher temperatures. These findings can be explained by the different structure of the active species or/and by coking these systems at different temperatures. In the case of less active catalysts supported on silicalite and silica gel, the formation of amorphous coke proceeds very slowly as compared with zeolite-based catalysts.

Calcination of the starting zeolite at higher temperatures (750°C) suppresses the catalyst coking as compared with the catalysts calcined at 520°C (Table 2). This fact correlates with the concepts of the role of Brøensted acidity in the process of coke formation and its suppression in the case of high-temperature dehydroxylation.

State of Iron and Gadolinium according to ESR Data

ESR data provide valuable information about the state and distribution of iron and gadolinium in the catalysts. Fe/H[Al]ZSM-5 samples were investigated earlier [19, 32]; moreover, the quantitative approach was used in the investigation of Fe^{3+} ions by ESR in [19]. The distribution and properties of Gd^{3+} ions in ZSM-5 zeolite and amorphous silica-alumina were studied in detail in [18, 34]. The results presented in these works facilitated the interpretation of the spectra.

Distribution and Properties of Iron Ions

The spectra of the initial sample with g = 4.3, 5.6, and 6.5 (Fig. 8, spectrum *1*) indicate that almost all the iron ions in the H[Al]ZSM-5 sample containing 0.5 wt % Fe are stabilized in the cationic positions of the zeolite as isolated Fe^{3+} ions in the local crystal field of low symmetry (tetrahedral and distorted tetrahedral coordination) [19]. Admission of air into the system leads to the broadening of low-field ESR signals, which is indicative of the accessibility of Fe^{3+} cations for the dipole–dipole interaction with O_2 molecules [19, 32]. The concentration of isolated coordinatively unsaturated Fe^{3+} ions remains approximately the same after increasing the iron content to 1.5% [19]. Oxidative calcination of the samples at 750°C does not change the distribution of iron ions. The distribution of iron ions in two other samples is dramatically different: in the case of 2% Fe/silicalite, only a small part of the iron is stabilized as isolated Fe^{3+} cations, whilst the most of the iron atoms form large α-Fe_2O_3 crystals characterized by a broad ESR signal (Fig. 8, spectrum *2*). The ESR spectrum of the 2% Fe/SiO_2 system contains no signals of paramagnetic moieties except for very weak low-field signals (Fig. 9, spectrum *3*). These signals can be attributed to trace amounts of Fe^{3+} ions introduced in the framework of SiO_2, because the admission of oxygen into the system does not lead to the broadening of these signals. The rest of the iron ions in 2% Fe/SiO_2 are stabilized in the form of small diamagnetic oxide particles. The difference in the distribution of aggregated iron oxide particles in silicalite and silica gel (Fig. 8, spectra *2* and *3*) may be caused by the different morphology of the samples: the external specific surface area of microcrystallites of silicalite is 20–30 m^2/g, and one would expect a much lower dispersion of iron oxide particles on silicalite compared to amorphous SiO_2, which is characterized by as high a specific surface area as 680 m^2/g. The ESR data provide evidence that the Fe/H[Al]ZSM-5 system may assist the stabilization of iron ions in specific forms, which are responsible for the catalytic activity of the samples in the oxidation of methane.

Modification of 0.5% Fe/H[Al]ZSM-5 by 1% Ag and further oxidative calcination at 520 or 750°C does not result in any changes in the intensity of the ESR signal of Fe^{3+} ions. So Ag^+ cations cannot displace isolated iron ions from the cationic positions in the channels of the zeolite. This result is in good agreement with the similarity of the catalytic properties of Fe/HZSM-5 and (Fe + Ag)/HZSM-5. The opposite results are observed in the case of the ions that can quantitatively displace Fe^{3+} ions from the cationic positions, for example Cu^{2+} in ZSM-5 [32].

State and Distribution of Gadolinium Ions

It was shown previously that the calcination of Gd/HZSM-5 in air at 500–900°C leads to the fine dispersion of a significant part of Gd^{3+} and their stabilization as isolated ions in several discrete coordination states [18, 34]. The isomorphous substitution of some part of Gd^{3+} ions in the framework of the carrier is evidenced by the appearance of ESR signals with $g = 5.8$ and 2.8 (Fig. 9). Beside the framework ions, tiny clusters of Gd^{3+} cations located in the channels of the HZSM-5 zeolite are formed. However, the ESR signal of these clusters cannot be observed in dry samples because of dipole–dipole broadening. However, hydration of the samples, which was previously proposed for the identification of such specifically stabilized lanthanum ions [18], leads to the disintegration of the cluster, and an intense ESR signal with $g = 1.98$ appears (Fig. 9, spectrum *1*). In contrast to HZSM-5, the surface of amorphous silica gel cannot provide the stabilization of such Gd^{3+} clusters, and no characteristic signal with $g = 1.98$ is observed in the wet Gd/SiO_2 sample (Fig. 9, spectrum *2*).

The presence of lanthanide ions dispersed in the zeolite matrix does not influence the stabilization of isolated Fe^{3+} ions in HZSM-5 and, vice versa, the ESR spectra of (Gd + Fe)/HZSM-5 (Fig. 10, spectrum *2*) is a simple superposition of ESR signals of Fe/HZSM-5 (Fig. 10, spectrum *1*) and Gd/HZSM-5. Comparison of normalized low-field components of the ESR signals shows that the intensity of the signal of Fe^{3+} ions decreases in the presence of gadolinium by some 15%, which is within the range of experimental error. Thus, the distribution and properties of iron ions in the calcined (Gd + Fe)/HZSM-5 catalyst are almost the same as in the case of monocomponent samples. A similar phenomenon of the “independent presence” in HZSM-5 was observed earlier for Gd + Cu [34] and Gd + Rh [35] systems. The ESR spectrum of the ternary (Gd + Fe + Ag)/HZSM-5 sample is equivalent to the spectrum of the (Gd + Fe)/HZSM-5 sample (Fig. 10, spectrum *2*). Thus, ESR data indicate that the modification of iron-containing zeolite with Gd^{3+} and Ag^+ does not influence the concentration and structure of the active Fe-sites. This result is in good agreement with the data of the catalytic tests.

CONCLUSIONS

(1) Modification of H[Al]ZSM-5 zeolite with iron and silver cations leads to the formation of catalytic sites that are active in the oxidation of methane by nitrous oxide, while the systems prepared on the basis of crystalline silicalite and amorphous SiO_2 demonstrate poor or no catalytic activity.

(2) Complete oxidation of methane with a 100% conversion and selectivity is observed on the Fe/HZSM-5 and Ag/HZSM-5 catalysts at temperatures higher than 350 and 450°C, respectively. A decrease in the reaction temperature and in the methane conversion is followed by the coking of the catalysts. The process of coke formation proceeds more intensively in the case of Ag/HZSM-5 and (Ag + Gd)/HZSM-5 catalysts than in the case of iron-containing catalysts.

(3) The catalytic properties of (Fe + Ag)/HZSM-5 are similar to those of Fe/HZSM-5. Introduction of Gd leading to a decrease in the catalyst acidity does not sig-

nificantly influence the activity and selectivity of the catalyst.

(4) In the case of the low-temperature partial oxidation of methane, the process of coke formation predominates, while such valuable products as methanol and formic acid are formed only in trace amounts. This result demonstrates the difficulties arising in the continuous process of catalytic production of oxygen-containing compounds from methane with appropriate yields and selectivities: the oxygen-containing compounds formed are more active than the initial CH_4 molecule and rapidly decompose into CO_2 and H_2O or coke.

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