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INFLUENCE OF THE CHEMICAL NATURE OF DEPOSITED METAL IONS ON THEIR CATALYTIC PROPERTIES IN OXIDATION OF METHANE BY NITROUS OXIDE

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The catalytic properties of deposited metal ions in the reaction between methane and nitrous oxide were studied. On the basis of a previously proposed mechanism for the heterogeneous-catalytic reaction, an interpretation was given for the observed activity and selectivity series with respect to the formation of methanol, carbon monoxide and dioxide. The determining factor regulating the catalytic properties in this system is the bond energy of metal ions with the adsorbed oxygen anion radicals 0⁻.

In the study of the reaction between CH_4 and N_2O in the presence of V_2O_5/SiO_2 we found [1] that low concentrations of vanadium ions in this catalyst promote the formation from N_2O of adsorbed oxygen anion-radicals O^- [2], which by reacting with methane give mild oxidation products (methanol, formaldehyde). To clarify the influence of the chemical nature of the

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Mm+	Degree of conversion, 7/0		Selectivity (in \mathcal{P}_0) with respect to			
	CH4	N ₂ O	CH ³ OH	нсно	со	CO₂
Ti ^{4+*}	1.8	21,4	13,8	0	0	86,2
Cr ³⁺	13,9	60,7	5,1	0	38,0	56,9
Mn ²⁺	16,9	56,3	1,4	0	28,2	70,4
Fe ²⁺	26,8	80,0	1,7	0	39,3	59,0
Fe ³⁺	25.7	83,3	1,1	0	29,7	69,2
Co ²⁺	20.5	64,7	0	0	25,0	75,0
Cu ²⁺	23.6	100,0	0,2	0,3	0	99,5
Zn^{2+}	21.2	81,5	0,6	0	37,3	62,1
Bi ³⁺	25.7	80,0	0.1	0	30.1	69.8

TABLE 1. Catalytic Properties of Metal Ions Deposited on Carbon in the Reaction between $\rm CH_4$ and $\rm N_2O$ at 773°K

*A small amount of ethanol was observed in the reaction products.

metal ions M^{m+} on the activity and selectivity of catalysts of this type, we studied in the present work the oxidation of methane by nitrous oxide in the presence of carbon samples containing equal concentrations of various ions M^{m+} (all samples contained also the same amount of iron ions, which comprise an ash impurity in carbons [3]). Transition metal ions of the IV-th period in the Mendeleev Periodic Table (and also Bi³⁺) were introduced in an amount of ~1 mmole/g into an AP-3 carbon by ion exchange from aqueous solutions of salts at room temperature.

The experiments were carried out in a flow type apparatus at low degrees of methane conversion; the reaction mixtures were analyzed chromatographically [1]. The composition of the initial gas mixture was (vol. %): $CH_4 - 20$, $N_2O - 15$, He - 63, $N_2 - 2$; flow rate 50 ml/min.

A 0.4 g portion of the catalyst was charged into the reactor. First it was activated in a helium current at the experimental temperature $(T = 773^{\circ}K)$ for 1 h, and then the reaction mixture was admitted. A brief heating up was observed (by 5-10°K), after which a stationary state was established. The data given below relate to stationary conditions. After prolonged operation (6 h) the catalysts became friable and brittle, and their activity decreased. The data obtained on fresh samples are satisfactorily reproduced (Fig. 1).

Table 1 shows that the catalysts used accelerate the partial oxidation of methane to methanol

$$CH_4 + NO_2 = CH_3OH + N_2 \tag{1}$$

and an extensive oxidation to carbon oxides

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

$$CH_4 + 4N_2O = CO_2 + 4N_2 + 2H_2O.$$
 (ITT)

On a copper-containing sample, an oxidation to formaldehyde also takes place

$$CH_1 + 2N_2O = HCHO + 2N_2 + H_2O,$$
 (IV)

while on a titanium-containing catalyst small quantities of ethanol are formed, i.e., an oxidative condensation takes place

$$2CH_4 + 2N_2O = C_2H_5OH + 2N_2 + H_2O.$$
 (V)

A substantial difference between the M^{m+}/C and V_2O_5/SiO_2 catalysts consists in that in the first case methanol is the main product of mild oxidation, while in the second case it is formaldehyde.

Figure 1 shows that the overall degree of conversion of methane (X_{CH_4}) is directly proportional to the degree of conversion of the oxidizing agent (X_{N_2O}) . We can obtain from this the mean ratio of the number of the converted moles of N_2O to the number of reacted moles of CH_4 : $\nu' \simeq 3.7$. On the other hand, the mean number of N_2O moles consumed in the oxidation of one mole of methane by reactions (I)-(V) can be determined from the relationship



Fig. 1. Dependence between degrees of conversion of CH₄ and N_2O (\circ - first, Δ - second series of experiments).

Fig. 2. Changes in the catalytic activity and selectivity in the series of the IV-th period transition metal ions.

$$\mathbf{v}'' = \sum_{i} \mathbf{v}_i S_i,\tag{1}$$

where v_i is a ratio of stoichiometric coefficients of N_2O and CH_4 in equations (I)-(V), S_i is the selectivity with respect to the corresponding product. The calculation according to Eq. (2) gives the mean value of v'' = 3.6. The fact that $v' \simeq v''$ leads to the conclusion that the decomposition of N_2O

$$2N_2O = 2N_2 + O_2 \tag{VI}$$

virtually does not take place, i.e., N_20 is consumed only on the oxidation of methane.

Figure 2 shows that the catalytic activity with respect to the overall transformation of the reagents increases on transition from Ti^{4+} to Cu^{2+} , i.e., with increase in the number of the d-electrons from 0 to 9. On transition to Zn^{2+} (the d¹⁰ configuration), the activity decreases. The selectivity with respect to the partial oxidation changes antibatically, while with respect to total oxidation symbatically to the overall activity. The activity and selectivity series have the following forms:

a) overall activity
$$-Cu$$
, $Fe > Zn > Co > Cr$, $Mn > Ti$; (VII)

b) selectivity with respect to methanol
$$-Ti > Cr$$
, Fe, $Mn > Zn > Cu > Co$. (VIIa)

The mechanism of the oxidation of methane by nitrous oxide can be represented according to the following scheme [1]:

1)
$$N_2O + M^{(m-1)+} \rightarrow M^{m+}O^- + N_2,$$

2) $CH_4 + M^{m+}O^+ \rightarrow CH_3M^{m+}OH^- \xrightarrow{\text{fast}} M^{m+}CH_3OH,$
3) $M^{m+}CH_3OH \rightarrow CH_3OH + M^{m+},$
4) $M^{m+}CH_3OH + M^{m+}O^- \rightarrow M^{(m-1)+}HCHO + H_2O,$ (VIII)
5) $M^{(m-1)+}HCHO \rightarrow HCHO + M^{(m-1)+},$
6) $M^{(m-1)+}HCHO + M^{m+}O^- \rightarrow M^{(m-1)+}HCOOH + M^{(m-1)+},$
7) $M^{(m-1)+}HCOOH \rightarrow CO + H_2O + M^{(m-1)+},$

8)
$$M^{(m-1)+}$$
 HCOOH + M^{m+} O⁺ \rightarrow CO₂ + H₂O + 2 $M^{(m-1)+}$

In the first stage are formed adsorbed anion-radicals 0, which are bound to the oxidized form of the catalyst cations M^{m+} , corresponding to the data in [2, 4]. In the second stage, methane reacts with 0 and the formed CH_3 and OH^- particles convert rapidly at elevated temperatures into adsorbed alcohols. During its desorption at the third stage, CH_3OH is formed, and formaldehyde on further surface oxidation at the fourth stage, which is desorbed in stage 5. The subsequent surface oxidation of the adsorbed formaldehyde, bound to the reduced form of the $M^{(m-1)+}$ cation, leads to the formation of extensive oxidation products via a surface formate, which was recorded in [5] by IR spectroscopy in the investigation of the reaction of methane with surface oxygen of metal oxides.

Mechanism (VIII) differs substantially from that proposed in [4]. In particular, the authors of [4] suggested that products of partial oxidation are formed with the participation of O⁻, while the products of extensive oxidation, are formed with the participation of O^{2^-} . We believe that the simplest and most natural possibility is that the reactive form O⁻ is capable of participating in all the stages leading to a partial and extensive oxidation. In this respect there are no experimental or theoretical grounds to draw a sharp boundary between stages 2-5 and 6-8, in the course of which the degree of oxidation of the products changes monotonically.

According to [4], methanol is formed during the hydrolysis of methoxyl groups CH_3O^- . This supposition is based on experimental conditions in [4], where large amounts of steam were added to the reaction mixture. Our experiments were carried out without the addition of H_2O , and the amount of water formed was insignificant because of low degrees of conversion, so that there was no need to introduce the stage of hydrolysis to the mechanism.

In [1], mechanism (VIII) was used to interpret the data for the oxidation of methane on a V_2O_5/SiO_2 catalyst. We used the same mechanism to explain the dependence obtained in the present work. According to (VIII), the overall catalytic activity r is determined by the rate of the first two stages, common for the formation of all the conversion products of methane. This corresponds to the classical scheme of alternate reduction - reoxidation of the surface, but with the participation of the adsorbed form of oxygen 0⁻, and not 0²⁻, as in most cases of oxidation by molecular oxygen [6]. For this mechanism

$$r = k_1 k_2 P_{N_2 O} P_{CH_4} / (k_1 P_{N_2 O} + v'' k_2 P_{CH_4}), \qquad (2)$$

where k_i are rate constants of the stages in scheme (VIII), P_i is partial pressure of the reagents. Since the reactivity of methane is low, while the values of P_{CH_4} , P_{N_20} are similar, then $k_1P_{N_20} \gg \nu''k_2P_{CH_4}$ and $r \simeq k_2P_{CH_4}$.

This means that the changes in the catalytic activity are determined by the changes in the rate constant of the second stage, in the course of which the $M^{m+}-0^{-}$ bond is split. Hence, with increase in the energy q of this bond, the catalytic activity should decrease.

It is difficult to verify this sequence because the data on the values of q are virtually unavailable (in contrast to the data on the values of the $M^{m+}-O^{2-}$ bond energies [6]). To surmount this difficulty, we exploited the fact, as known from [6], that the catalytic decomposition of N₂O on metal oxides proceeds by the mechanism

1)
$$N_2O + M^{(m-1)+} \to M^{m+}O^{-} + N_2.$$

2) $N_2O + M^{m+}O^{-} \to N_2 + O_2 + M^{(m-1)+}.$
(IX)

The first stage of this mechanism is identical with the first stage of mechanism (VIII), while the second stages of the two mechanisms are similar. In the case of mechanism (IX), the catalytic activity is determined by stage 2, whose rate decreases with increase in q [6], so that we should expect the catalytic activity in the oxidation reaction of methane to increase with increase in the activity of the corresponding metal oxides with respect to reaction (VI). Figure 3 shows that in fact this takes place. Thus, the activity series of (VII) is explained mainly by the difference in the strength of the M^{m+}-O⁻ bond.

We should note the similarity between this series and the activity series of zeolites Y, containing transition metal ions [8]

$$\operatorname{Cu} Y > \operatorname{Fe} Y > \operatorname{Co} Y, \ \operatorname{Cr} Y > \operatorname{Mn} Y, \tag{X}$$



Fig. 3. Dependence of the catalytic activity of the M^{m+} ions in the oxidation of methane by nitrous oxide on the activity of the corresponding oxides in the decomposition of N₂O (r_{N_2O} is the specific catalytic activity at 723°K [7]).

Fig. 4. Comparison of selectivity with respect to methanol with $\log r_{\rm N_{2}O}.$

in the oxidation reaction of hydrogen by molecular oxygen. This analogy can be explained by the fact that in the last case, the radical forms of the adsorbed oxygen also participate in the catalytic process, since the formation of 0^{2^-} from 0_2 requiring a multielectronic transfer is hindered by the disengagement of M^{m+} ions in the metal zeolite.

Let us consider the characteristics of the changes in the selectivity with respect to various products. According to mechanism (VIII), the equations for the selectivity have the form

$$S_{\rm CH_{s}OH} = k_3/(k_3 + k_4\theta),$$
 (3)

$$S_{\rm HCHO} = [k_4 \theta / (k_3 + k_4 \theta)] \cdot [k_5 / (k_5 + k_6 \theta)], \tag{4}$$

$$S_{\rm CO} = [k_4 \theta / (k_3 + k_4 \theta)] \cdot [k_4 \theta / (k_5 + k_6 \theta)] \cdot [k_7 / (k_7 + k_8 \theta)], \tag{5}$$

$$S_{\text{CO}_2} = [k_4 \theta / (k_3 + k_4 \theta)] \cdot [k_5 \theta / (k_5 + k_6 \theta)] \cdot [k_5 \theta / (k_7 + k_5 \theta)]$$
(6)

 $(k_i \text{ are reaction rate constants}, \theta \text{ is degree of filling the surface by oxygen})$. In their makeup, expressions (3)-(6) are similar to the equations for selectivity with respect to the products of o-xylene oxidation by molecular oxygen [9].

The experimental data show that formaldehyde is not detected in the products with most of the catalysts we studied (Table 1). This means that its desorption proceeds much more slowly than the surface oxidation ($k_5 \ll k_6\theta$; S_{HCHO} \approx 0). At $\theta \approx$ 1, equations (3)-(6) become simplified

$$S_{\rm CH_3OH} = k_3 / (k_3 + k_4),$$
 (7)

$$S_{\rm CO} = [k_4/(k_3 + k_4)] \cdot [k_7/(k_7 + k_8)], \tag{8}$$

$$S_{\rm CO_2} = [k_4/(k_3 + k_4)] \cdot [k_8/(k_7 + k_8)]. \tag{9}$$

Assuming that, in the first approximation, the changes in the selectivity in the series of the catalysts of the same type being compared are preferentially changes in the bond energy q of the adsorbed reactive oxygen, on which only constants k_4 , k_8 are dependent (they decrease with increase in q), the following deductions are obtained: the selectivity with respect to the least oxidized product (CH₃OH) should increase; with respect to the most oxidized product (CO₂) it should decrease; and with respect to the product with an intermediate degree of oxidation (CO), it should pass through a maximum with a monotonic increase in q. To verify these deductions, we shall use, as above, the values of $\log r_{N_2O}$, which change antibatically with q. In this case we should expect that with increase in $\log r_{N_2O}$, the value of S_{CH_3OH}



Fig. 5. Dependence of selectivity on logr_{N20}: a) with respect to CO₂; b) with respect to CO.

should decrease, S_{CO_2} should increase, and S_{CO} should pass through a maximum. Figs. 4 and 5 show that all these deductions are verified, and so interpretation is found for the selectivity series.

The activity with respect to the overall process increases with increase in $\log r_{N_2O}$ (Fig. 3). Comparison of this dependence with those shown in Figs. 4, 5 makes it possible to understand the symbatic change in X_{CH_4} and S_{CO_2} and the antibatic change in X_{CH_4} and S_{CH_3OH} , noted as an empirical regularity at the beginning of the article (Fig. 2). This change is caused by the influence of the general physicochemical property of catalysts, namely, their adsorption affinity to oxygen, on the activity and selectivity. The above analysis is necessarily only approximate. In a more accurate analysis, we have to take into account the following: the possibility of simultaneous participation of various forms of the adsorbed oxygen in the reaction; the probability of additional oxidation of mild oxidation products at high degrees of conversion; combined influence of the bond strength of oxygen and the acidity of the surface on rate constants of stages 2-8, etc. To solve these problems, the collection is necessary of experimental data which have a kinetic character, and which also reflect the physicochemical properties of the intermediate surface compounds. All the same, our results lead us to assume that the proposed mechanism and approach to the treatment of the empirical regularities can serve as a basis for further, more comprehensive study of this reaction.

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