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Oxidative Synthesis of Higher Hydrocarbons from Methane on Zeolites

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The rate and selectivity of oxidative synthesis of higher hydrocarbons from methane have been studied as functions of the chemical composition and structural type of zeolite catalysts applied and the nature of oxidants (O_2, N_2O, NO, NO_2, SO_3). The greatest yield of higher hydrocarbons has been received in the presence of N_2O. The interaction of methane with different zeolites has been investigated by NMR and IR spectroscopy methods. Methane activation during oxidative synthesis was shown to occur on zeolite acid sites. The mechanism of methane activation and conversion on pentasil zeolites has been proposed. © 1989 Academic Press, Inc.

INTRODUCTION

Many attempts have been made recently to find ways to produce higher hydrocarbons (HHC) from methane. The most widespread method of methane chemical processing is steam conversion, in which a mixture of hydrogen and carbon monoxide is formed. HHC can be obtained from this mixture either directly (Fisher–Tropsch process) or through the steps of methanol synthesis (Mobil process) (*1*). The methods on the whole are multistep, which worsens their economic and technological characteristics. Benzene formation was observed (*2*) when methane pulses had been passed above Pt-containing zeolites of pentasil type. Its yield did not exceed 6%, which seems to be due to thermodynamic restrictions. Recently a single-step synthesis of aromatic hydrocarbons from methane using boron nitrides and carbides as catalysts has been proposed (*3*). The process was performed at 1300 K.

According to thermodynamics, a considerable yield of higher hydrocarbons during methane conversion at lower temperatures can be attained only in the presence of oxidant. Such a process using transition metal oxides was first proposed in (*4*). However, in that case the oxidative conversion of methane seems more stoichiometric than catalytic.

One way to solve the problem is the application of bifunctional catalysts. If in the course of methane oxidation intermediate products of partial oxidation, methanol for example, are formed, the addition of a catalyst with acid–base properties would provide methanol conversion into liquid hydrocarbons. Zeolites of pentasil type, whose activity in the synthesis of liquid hydrocarbons from methanol is well known (*1*), may serve as such catalysts. The probable scheme of this process is demonstrated in Fig. 1. On the whole the catalyst must contain components which are active in the oxidation reaction at step 1 (*KO*) and also some zeolite component (*Z*) which carries out conversion via an acid–base mechanism at step 2. Successful oxidative synthesis of higher hydrocarbons from methane in the presence of various oxidants (O_2, N_2O, NO, NO_2, SO_3) on zeolite catalysts has been carried out in our earlier investigations (*5–7*) and in recent works by others (*8, 9*). This paper describes catalytic properties of zeolites of varying structure and chemical composition in this process.

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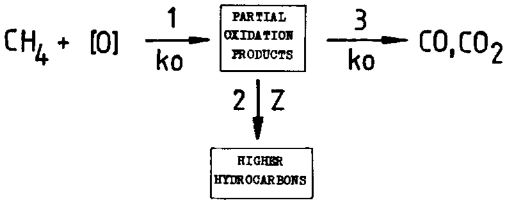

FIG. 1. Scheme of oxidative conversions of methane on bifunctional catalysts.

EXPERIMENTAL

Zeolites of pentasil type were prepared by hydrothermal synthesis according to (*10*). Faujasite and mordenite zeolites were prepared by VNIIINP (All-Union Institute of Oil Processing) on commercial scale. Decationation of zeolites was carried out by ion exchange with an ammonium chloride solution followed by drying and calcination of the samples at 773 K. Dealumination of mordenites was performed as described in (*11*) by treating zeolites with hydrochloric acid; dealumination of faujasites was carried out by treating them with vapor of silicon tetrachloride according to (*12*). The chemical composition and crystallinity (CZP) of decationated zeolites used in this work are given in Table 1. Designations of zeolite samples in this work are as follows: "P-28," where P is the structural zeolite type (P, pentasil; M, mordenite; F, faujasite). The numbers in these designations correspond to the value of the SiO_2/Al_2O_3 ratio in the samples derived from the chemical analysis. To examine the influence of iron oxide admixtures in zeolites on their catalytic properties, the pentasil series with varying Fe_2O_3 contents was prepared by impregnation of P-28 pentasil powder with $Fe(NO_3)_3$ solution at pH 1 followed by drying of zeolite and calcination for 2–4 h at 773 K.

Catalysts were prepared by pelleting zeolite powders without binder at a pressure of 2×10^8 N m^{-2}. The pellets were crushed and sized between sieves with 0.5- and 0.25-mm holes. It was established by separate experiments that the variation of average diameter of catalyst particles in this range had no effect on the reaction rate or selectivity.

IR spectroscopic investigations of zeolites were performed on a Specord-IR-75 spectrometer at 3000–4000 cm^{-1} after calcination of catalysts at 723 K in oxygen for 2 h. Methane was adsorbed under pressures of 27–33 kPa at temperatures of 103, 298, and 603 K. Methane enriched with 90% ^{13}C was used for NMR studies performed at room temperature. Methane was adsorbed under 0.27–93 kPa and at 293 K. NMR MAS spectra were recorded on a CXP-300 Bruker spectrometer.

Methane and oxidants of 99.99% purity grade were used. No other reagents, diluters, or gas promoters were applied. Catalytic tests were performed in a flow-circulation gradientless apparatus with a quartz reactor having a volume of 50 cm^3 at 673 K under atmospheric pressure. Composition of the inlet and outlet mixtures was analyzed by gas chromatography; for product

TABLE 1

Chemical Composition of Decationated Zeolites Studied

Sample	Content in mass%[a]				
	Na_2O	SiO_2	Al_2O_3	Fe_2O_3	CZP[b]
P-28	0.05	79.9	4.82	0.14	100
P-38	0.09	84.6	3.81	0.28	100
P-48	0.05	86.9	3.05	0.24	83
P-84	0.05	88.9	1.79	0.14	98
P-121	0.06	91.9	1.29	0.19	96
P-176	0.05	91.4	0.89	0.21	100
F-4.7	0.6	51.8	18.9	0.07	100
F-13	0.6	74.6	9.5	0.04	38
F-22	0.2	88.2	6.8	0.03	50
M-12	0.8	74.6	10.5	0.09	100
M-18	0.55	70.7	6.57	0.07	80
M-41	0.16	83.0	3.43	0.04	80

[a] The difference between sums of values listed and 100% corresponds to adsorbed water and organic template.

[b] Content of the crystalline zeolite phase in the samples derived from X-ray data.

identification, mass spectrometer was used. An inlet methane-to-oxidant molar ratio of not less than 5 was maintained to provide an excess of methane. This made the changes of methane concentration nonessential, which allowed us to ignore the changes of the reaction mixture volume and use the rate equation

$$\frac{v}{m}([O]_{\text{in}} - [O]_{\text{out}}) = W, \quad (1)$$

where $[O]_{\text{in}}$ and $[O]_{\text{out}}$ are the oxidant inlet and outlet concentrations, respectively (mol/m^3), v is the space velocity of the reaction mixture (m^3/s), m is the catalyst charge (kg), and W is the reaction rate (mol s^{-1} kg^{-1}). The $[O]_{\text{in}}$ was varied from 0.1 to 7.0 mol/m^3, the v/m ratio from 9×10^{-5} to 20×10^{-5} m^3 s^{-1} kg^{-1}. Changes in m did not affect the W value, as was shown by control experiments. This means that no reaction occurs in the void reactor volume. No methane conversion was detected in an empty reactor or in one with a catalyst but without oxidant in the reaction mixture. The rate of pure N_2O decomposition in the presence of our most active catalyst P-28 is negligible in comparison with N_2O consumption in the presence of methane.

The N_2O consumption rates (W_i) to various carbon-containing products were calculated using the equation

$$W_i = P_i[Y]\frac{v}{m}, \quad (2)$$

where $[Y]$ is the outlet concentration of the ith component (mol/m^3) and P_i is the stoichiometric coefficient from the respective equation,

$$k_iCH_4 + P_iN_2O \rightarrow Y + P_iH_2O + P_iN_2.$$

For each catalyst we chose the $[O]_{\text{in}}$ and v/m ratio to provide the $[O]_{\text{out}}$ of 0.1 mol/m^3. The W values derived from Eqs. (1) and (2) at this oxidant concentration were used as a measure of the catalytic activity of the samples.

EXPERIMENTAL RESULTS

1. Methane Oxidation with O_2

The composition of products obtained in methane oxidation by O_2 in the presence of the P-28 zeolite is shown in Table 2. The products of complete oxidation, ethane, ethylene, hydrogen, and coke on zeolite are formed. Carbon oxides were the main reaction products. Zeolites of varying composition were tested (Table 3). As can be seen, the reaction rates in the presence of pentasils with different SiO_2/Al_2O_3 molar ratios are practically the same. However, the selectivity toward HHC increases with increasing Al_2O_3 content in zeolites of pentasil type. The substitution of hydrogen cations by sodium cations in pentasil leads to a considerable increase in reaction rate, while the formation of higher hydrocarbons

TABLE 2

The Composition of Products of Methane Interaction with Oxygen on P-28 Zeolite

Product	Concentration (mol/m^3)
O_2	0.10
CO	1.12
CO_2	0.65
H_2O	3.54
H_2	0.07
CH_4	36.1
C_2H_4	0.004
C_2H_6	0.025
Conversion (%)	
Methane	4.85
Oxygen	96.9
Selectivity of formation from methane (%)	
Carbon oxides	97.0
HHC	3.0

Note. Reaction temperature is 873 K; oxygen input concentration, 3.13 mol/m^3; catalytic charge, 0.01 kg.; volume reaction mixture velocity, 0.66×10^{-6} m^3/s.

TABLE 3

The Rate and Selectivity of Methane Oxidation by Oxygen on Zeolites of Different Types and Chemical Compositions

Zeolite	Oxygen consumption rate (10^5 mol/(s kg))	Selectivity of product formation from methane (%)	
		Carbon oxides	HHC
P-176	21	99.9	0.1
P-121	21	99.0	1.0
P-84	16	98.2	1.8
P-48	16	97.5	2.5
P-38	17	97.4	2.6
P-28	20	97.0	3.0
Na-P-28	213	100	0.0
F-4.7	13	100	0.0
M-12	15	100	0.0

Note. The reaction conditions are listed in Table 2.

and coke ceases. In the presence of decationated mordenites and faujasites neither HHC nor coke was formed; the reaction results in complete oxidation of methane.

Methane interaction with different oxidants over the P-28 pentasil was also investigated. Application of NO, NO_2, or SO_3 leads to the formation of only carbon oxides from methane. The rates of oxidant consumption in reaction with methane on the P-28 pentasil are listed in Table 4. It can be seen that nitrous oxide is the most active. The use of this oxide allows us to obtain higher hydrocarbons from methane with a selectivity up to 90%. The product composition of this reaction in the presence of the P-28 catalyst is given in Table 5.

TABLE 4

The Rates of Consumption of Various Oxidants in Reaction with Methane on the P-28 Zeolite

Oxidant	Products	Reaction rate (mol/(s kg))	Energy of oxygen atom abstraction (kJ/mol)
N_2O	HHC, H_2O, N_2	60×10^{-5}	128
NO_2	CO_2, H_2O, NO, N_2	15×10^{-5}	267
SO_3	CO_2, H_2O, SO_2, H_2S	2.1×10^{-5}	411
O_2	CO_2, H_2O, C_2H_6	3.2×10^{-6}	464
NO	CO_2, H_2O, N_2	1×10^{-8}	602

Note. The reaction temperature was 673 K; the oxidant outlet concentration, 0.1 mol/m^3.

2. *Methane Oxidation with Nitrous Oxide*

The investigation of catalytic properties of pentasils with different Al_2O_3 contents (Fig. 2) indicates that a decrease in Al_2O_3 content results in a corresponding decrease of catalytic activity. As hydrogen cations are substituted by sodium cations, the catalytic activity of pentasils decreases (Fig. 3). This allows us to conclude that zeolite active sites are related to the presence of aluminum cations and arise upon decationation.

Faujasites and mordenites containing more Al_2O_3 than pentasils were expected to be more active catalysts. Investigations, however, proved their activity to be essentially lower than that of pentasils (Fig. 4). Higher hydrocarbons do not form in the presence of faujasites and mordenites, the reaction products being only carbon oxides and water. The investigations of dealumi-

TABLE 5

The Selectivity of Methane Transformation in the Presence of N_2O

Product	Concentration (mass%)	Composition of HHC fraction	
		Product	Concentration (mass%)
N_2	19.1	C_2H_4	2.51
CO	0.20	C_2H_6	0.19
CO_2	0.81	Benzene	0.65
H_2O	11.5	Toluene	2.69
N_2O	0.66	Aromatics C_8	19.4
CH_4	62.7	C_9	9.5
HHC	5.03	C_{10}	6.7
		Naphthalene	16.0
		Methylnaphthalenes	16.9
		Dimethylnaphthalenes	25.4

Methane conversion—9.64%
N_2O conversion—98.2%
Selectivity of methane conversion toward HHC—87.5%

Note. Catalyst, P-28, reaction temperature, 673 K; catalyst charge, 0.01 kg; volume velocity of reaction mixture, 1.08×10^{-6} m^3/s. Inlet concentration of N_2O, 5.75, and of CH_4, 35.85 mol/m^3.

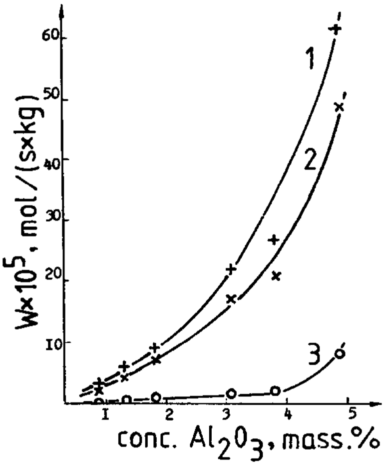

FIG. 2. Plot of N_2O consumption rate (*W*): (1) total; (2) for the formation of HHC; and (3) for the formation of carbon oxides vs alumina content in pentasils used as catalysts.

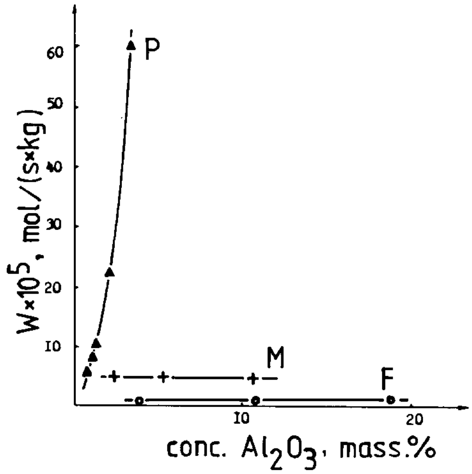

FIG. 4. Plot of total N_2O consumption rate (*W*) in reaction with methane vs. alumina content in zeolites of different structural types used as catalysts (P, pentasils; M, mordenites; F, faujasites).

nated faujasites and mordenites indicate that a decrease in Al_2O_3 content down to the value typical for pentasils does not enhance the catalytic activity of these samples.

Transition metal oxides are generally considered to be the most active catalysts for oxidative reactions. Chemical analysis of zeolite catalysts applied indicated the iron oxides to be the most abundant admixture and to be able to play the role of *KO* in the course of bifunctional oxidative synthesis (see scheme in Fig. 1). From the data of Table 6, it can be seen that introduction of iron oxide into zeolite leads to insignificant changes in catalytic activity and selectivity. One may conclude that admixtures of iron oxides in zeolites over the concentration

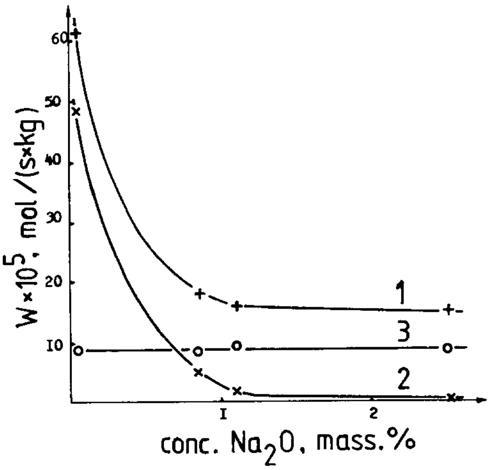

FIG. 3. Plot of N_2O consumption rate (*W*): (1) total; (2) for the formation of HHC; and (3) for the formation of carbon oxides vs sodium oxide content in pentasil P-28 used as catalyst.

TABLE 6

The Rate and Selectivity of HHC Formation from Methane in the Presence of N_2O on Pentasils Containing Iron Oxide

Catalyst	Fe_2O_3 content (mass%)	Rate of N_2O consumption (10^5 mol/(s kg))	Selectivity of HHC formation from methane converted (mass%)
P-28	0.05	59	91
P-28	0.14	60	87
P-28	0.98	55	86
P-28	5.11	65	78

Note. The reaction temperature was 673 K; catalyst charge, 0.01 kg, outlet N_2O concentration, 0.1 mol/m^3. Methane conversion was from 5 to 10%.

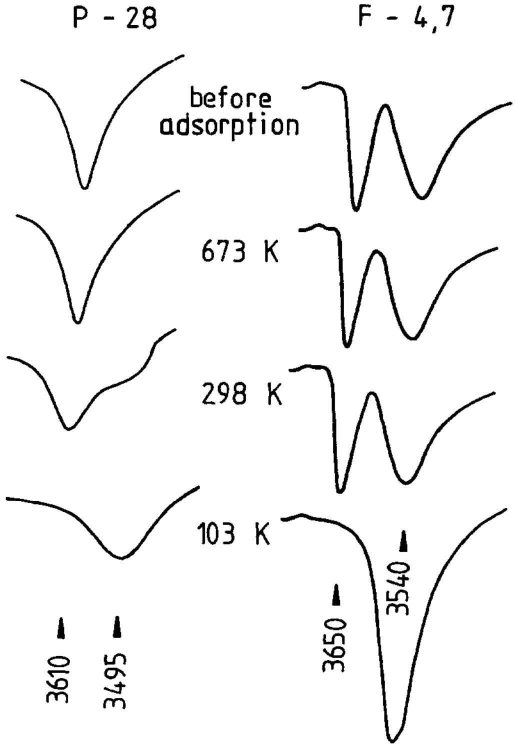

FIG. 5. Variations in IR absorption bands ascribed to zeolite hydroxyl groups upon methane adsorption on zeolite.

range investigated are not responsible for their catalytic activity.

3. *NMR and IR Investigations of Methane Adsorbed on Zeolites*

IR spectra in the region of vibration frequencies of zeolite OH groups are given in Fig. 5. Methane adsorption on zeolites leads to the decrease of the frequency of these vibrations. Such an effect is established at 103 K for all types of decationated zeolites investigated and only for pentasils at room temperature. A greater shift of vibration frequencies of OH groups in IR spectra for pentasil than for faujasite after methane adsorption at 103 K has been found. On the basis of these observations, the interaction between methane and zeolite OH groups is assumed to result in the formation of the H bond, which is stronger on pentasil than on faujasite.

NMR investigations of $^{13}CH_4$ adsorbed on pentasil showed the signal from ^{13}C nuclei to be shifted toward the lower field relative to the signal of gaseous methane (Fig. 6). Methane adsorption on decationated pentasils decreases the spin–spin interaction constant (^{13}C–^{1}H) which indicates the lengthening and weakening of the C–H bond in methane. The chemical shift of the ^{13}C signal increases with increasing Al_2O_3 content and decreasing Na_2O content in pentasils (Fig. 7). Thus, zeolite active sites whose interaction with methane is detected by NMR are related to Al cations and appear during decationation. Decationated faujasite and mordenite, however, are inferior to pentasils in the value of the chemical shift. No change in the spin–spin interaction constant was observed during methane adsorption on the faujasites and mordenites. Considerable changes in NMR spectra of adsorbed as compared to gaseous methane occur only on zeolites which show a higher selectivity in oxidative synthesis of HHC from methane. Thus we may suppose that the interaction between methane and zeolite active sites observed by NMR is the first step of methane catalytic oxidation.

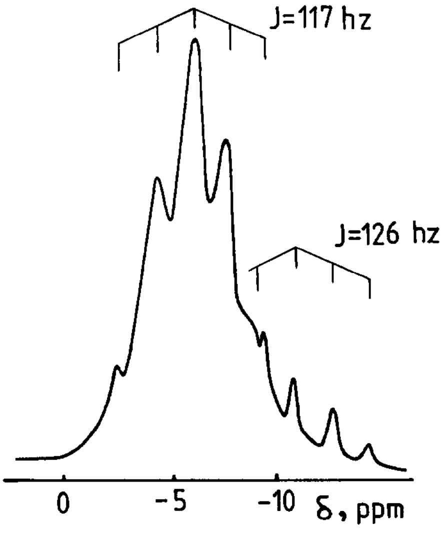

FIG. 6. The $^{13}CH_4$ NMR MAS spectrum of methane adsorbed on the P-28 zeolite. 10^{21} methane molecules per gram of zeolite were adsorbed.

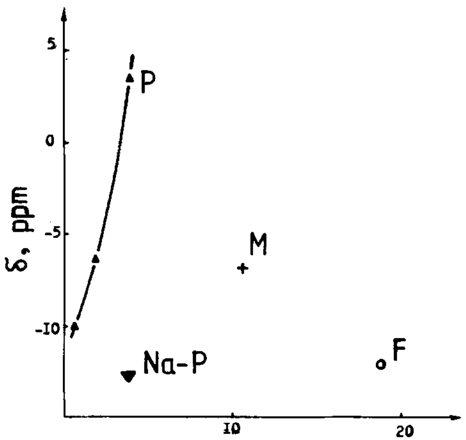

FIG. 7. Plot of chemical shift in the ^{13}C NMR spectrum of adsorbed methane vs. alumina content. 10^{20} molecules per gram of zeolite were adsorbed.

DISCUSSION

The first question arising from our observation is What kinds of catalytically active sites take part in the reaction under study? The best of our catalysts was not loaded with any transition metal compounds. One can presume that admixtures of said compounds, especially of iron oxides, form the active sites. Let us reconsider the scheme in Fig. 1 to answer this question.

If the catalytic activity in the first step is related to transition metal admixtures working as *KO* the rate of reagent consumption must not depend on sodium or aluminum content in zeolite. The change in concentration of acid sites would affect only the rate of the second step and therefore only the process selectivity. This assumption contradicts our observation: the more aluminum and the less sodium zeolite contains, the higher its catalytic activity. It prompts us to conclude that not only *KO* but also some sites connected with Al ions and arising upon decationation take part in the first step. Acid sites of pentasils fit these requirements. Both reagents can be activated in the first step in general. However, the increase of the N_2O activation rate on acid sites should lead to the increase of both the first and the third steps and the selectivity toward HHC should be low. The increase of the methane activation rate leads to the increase of the rate of the first step only and to high selectivity of the HHC formation. This is in compliance with our experimental data. So we must admit that CH_4 activation is more probable as the limiting step than N_2O activation. The low rate of N_2O decomposition on P-28 catalyst and the NMR data presented here are additional facts supporting this supposition.

Decationated pentasils with high alumina contents are much more active in the reaction investigated than faujasites and mordenites. This can be attributed to the peculiarities of zeolite structures. One should consider that the adsorption potential in a narrow-pore system cn lower the activated complex formation energy and fasten the reaction. The smaller the pore size, the greater must be the adsorption potential. Pentasils have the narrowest pore system among the zeolites investigated and their high catalytic activity can readily be explained using this approach. An explanation of the high catalytic activity of pentasils in the pentane cracking reaction similar to that for faujasites and mordenites has been proposed recently by Derouane and co-workers (*13*), as have pentasil advantages in the interaction with adsorbates detectable by the NMR technique (*14*). Barthomeuf (*15*) has also emphasized that the chemical environments of zeolite acid sites should affect their acidic and catalytic properties.

The following pictures of methane activation and transformation can be proposed for consideration (Fig. 8). Methane adsorption on zeolite acid sites results in polarization of its molecule and in increase of the negative charge of one of the hydrogen atoms. A high adsorption potential in narrow pentasil channels can support such polarization. A partially negatively charged hydrogen atom of a methane molecule becomes accessible to attack by the N_2O

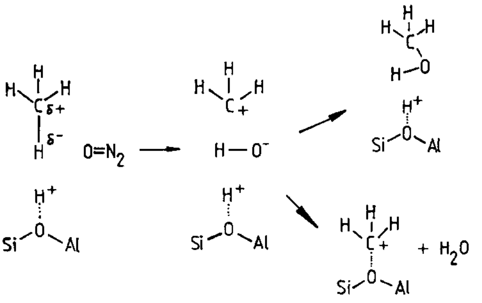

FIG. 8. Interaction of the polarized methane molecule with the oxidant.

molecule followed by decomposition of this oxide. The resulting OH^- anion can interact with CH_3^+, yielding methanol, or with the acid site proton, yielding water. In the latter case an alkoxide group must remain instead of the acid site. This seems to be the completion of the first step of the methane conversion scheme presented in Fig. 1. The absence of methanol from reaction products can be explained by consideration of the higher rate of its further conversion into liquid hydrocarbons. It should be noted that carrying out oxidative synthesis from methane and nitrous oxide on pentasils under conditions milder than ours, the authors of (*8*, *16*) observed methanol formation.

This scheme involves the abstraction of the oxygen atom from the oxidant molecule. The more energy such abstraction requires, the higher is the activation energy and the lower is the reaction rate. A good correlation between the energy of oxygen atom abstraction from the oxidant molecule and the reaction rate (Table 4) suggests that this abstraction is the limiting step.

Considering the scheme in Fig. 1, one can assume that the decrease in oxidant reactivity should decrease the rate of step 3 compared to that of step 2 and enhance the selectivity of HHC formation. However, it has been shown in our investigations that the most active oxidant N_2O (see Table 4), shows the greatest selectivity. Thus suggests that the preliminary scheme in Fig. 1 should be modified. Apparently, we should introduce step 4 of the complete methane oxidation through intermediates incapable of reacting in step 2 and step 5 of complete oxidation of HHC:

$$\begin{tikzcd}
\mathrm{CH} + (O) \arrow[r, "1"] \arrow[rr, bend left, "4"] & \text{partial oxidation products} \arrow[r, "3"] \arrow[d, "2"] & \text{carbon oxides} \\
& \text{HHC} \arrow[ur, "5"'] &
\end{tikzcd}$$

Assuming steps 3, 4, and 5 to proceed via a mechanism different from that proposed for the first step (through the radical-chain mechanism, for example) we can consider the N_2O which is the most active in the first step to be at least of the same reactivity in steps 3, 4, and 5 as oxygen and other oxidants investigated. Thus, the rate of the first step with O_2 and other oxidants is rather low and cannot compete with steps 3, 4, and 5-, and therefore the selectivity toward HHC is poor. One must take into account that in the methane oxidation reaction on transition metal oxides (*17*, *18*) and on metal-loaded zeolites (*19*), N_2O as oxidant is less active than O_2. This indicates that the methane oxidation mechanism on acid sites is unique and different from the oxidation mechanism on oxides of transitional elements.

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