Hydrocarbon conversion on ZSM-5 in the presence of N_2O: relative reactivity

S.N. Vereshchagin [*], N.P. Kirik, N.N. Shishkina and A.G. Anshits

Institute of Chemistry and Chemical Engineering, K. Marx 42, Krasnoyarsk 660049, Russia
E-mail: root@au.krasnoyarsk.su

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Conversions of methane, ethane, propane, benzene and hydrogen were studied on HZSM-5 at 418 °C using binary mixtures $R1:R2:N_2O:He$ (where R1, R2 are substances under study). Relative reactivities were determined, and it was shown that the rates of conversion of hydrocarbons are determined by the strengths of C–H bonds (H–H for hydrogen).

Keywords: ZSM-5, alkanes, relative reactivity

1. Introduction

It is known that the interaction of N_2O with ZSM-5 type zeolites produces an extremely active surface oxygen species discovered by Vereshchagin et al. [1], which was called α-oxygen [2]. The α-oxygen is capable of converting ethane to ethylene with 96–98% selectivity, reacts with methane at ambient temperatures to give methanol or converts benzene to phenol at moderate temperatures [1,3,4]. To understand the origin of this extraordinary activity and selectivity it is necessary to study both the active sites for N_2O activation (decomposition) and the details of hydrocarbon interaction with α-oxygen. There is some information concerning the nature of N_2O activation sites, which are believed to be Fe-containing extra-framework species [5]; acid centres of the zeolite surface are also thought to be able to activate N_2O [6], but there is a lack of data concerning the chemical properties of α-oxygen. The objective of the present paper is to study relative reactivities of different hydrocarbons with respect to surface α-oxygen.

2. Experimental

The sample of NaZSM-5 type zeolite (according to XRD) with molar ratio $SiO_2/Al_2O_3 = 33$ was used as a starting material. Zeolite was converted to NH_4-form by stirring in a 1 N aqueous solution of NH_4Cl at 70 °C. The material obtained was filtered, washed with water at room temperature, dried at 100 °C and calcined at 500 °C for 3 h and at 900 °C for 1 h. The content of sodium and iron was determined by elemental analyses after dissolution of the zeolite and was found to be 0.01 and 0.055 wt%, respectively. Zeolite powder was pressed (70 atm/cm^2), pellets were crushed and a 0.25–0.4 mm fraction was used for catalytic experiments.

Methane, ethane, propane, helium and hydrogen used were 99.98% purity, dinitrogen monoxide was medically pure grade. Gases were premixed with helium to obtain the desired composition. Benzene was introduced into the feed by means of a saturator kept at 0 °C. Initial concentrations of feeds were: N_2O (5–15 vol%), two substrates (1–15 vol% each, e.g., methane and ethane) and helium (balance).

Catalytic runs were carried out in a conventional catalytic set-up with stationary catalyst bed (about 100 mg of catalyst) in a quartz tubular reactor, (i.d. 6 mm). Before a catalytic run the sample was pre-treated in an oxygen flow at 550 °C for 1.5 h. The sample was then cooled to 418 °C and the oxygen flow replaced by the feed (0.5–2 $cm^3\,s^{-1}$ STP). The feed flow was varied to reach different initial conversions (usually 5–30%) of the most active reactant, except for C_2H_6–CH_4–N_2O feed where 20–60% of ethane conversion was necessary to obtain simultaneously 2–9% conversion of methane. Analyses of the reactants and products formed were carried out using an on-line gas chromatograph equipped with both packed (molecular sieve CaA and Porapak Q, TC detector) and capillary columns (50 m SE-30, 10 m Carbowax 20M, FID detector). Relative reactivities of hydrocarbons were calculated from the changes of concentration of the reacting hydrocarbons as described below.

3. Results and discussion

Table 1 shows the principal and minor products which are formed when individual hydrocarbons react with N_2O on the zeolite under study. In accordance with the data published earlier [1,2], α-oxygen is very reactive towards hydrocarbons, and 96–99% selectivity to principal products at conversions lower than 10% is observed in this study. Products listed in table 1, which are formed with about

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[*] To whom correspondence should be addressed.

Table 1
Principal and minor products formed on ZSM-5 at 380–418 °C from different hydrocarbons in the presence of N_2O (conversion less than 10%).

Hydrocarbon	Main product, selectivity (%)	Minor products	Refs.
Methane	CO, CO_2	Aromatic hydrocarbons	This work
Ethane	C_2H_4 (90–98)	C_3–C_6 olefins, aromatic hydrocarbons, CO_2	[1]
Propane	C_3H_6 (90–98)	C_4–C_6 olefins, aromatic hydrocarbons, CO_2	This work
Benzene	C_6H_5OH (>95)	CO_2	[2], this work

100% selectivity, must be treated as the primary products of α-oxygen reaction with hydrocarbons. The conversion of hydrocarbon drops rapidly with time on stream indicating deactivation of the catalyst, the rate of activity decrease being different for distinct hydrocarbon feeds (from 1.5 to 4 times for the first 20 min of run).

A quantitative measure of reactivity of hydrocarbon RH towards surface active oxygen [O] is the kinetic constant k of the reaction $[\mathrm{O}] + \mathrm{RH} \xrightarrow{k}$ products. For the process studied the reactivity of a given hydrocarbon cannot be characterised by the value of the total rate of individual RH conversion when the single reactant feed ($\mathrm{RH}:N_2O:\mathrm{He}$) is used, because of the complex multi-stage character of the process. The same is true for relative reactivity calculated as a ratio of conversion rates of substances.

To calculate the value of k from experimental data it is necessary to know a kinetic low for the total process of hydrocarbon conversion. As it was shown for CO oxidation by N_2O over FeZSM-5 at 350–440 °C [7], the kinetic equation included at least one additional kinetic constant which corresponded to the reaction of N_2O decomposition, $N_2O \rightarrow N_2 + [\mathrm{O}]$. In our case the fast changes of activity make the values of k, calculated in such a way, inaccurate and not reliable.

It should be pointed out that selectivity remains constant with time on stream, which means that there are no changes in the mechanism of the reaction during deactivation and the decrease of activity is caused only by the decrease of the number of active sites. For this case it is possible to determine the relative reactivity of hydrocarbons using the well known approach for determination of relative rate constants for parallel reactions from the data of simultaneous conversion of two substances under study [8].

Conversion of feeds containing two hydrocarbons, N_2O and helium, leads to the formation of more complex mixtures, though the principal products remain the same. For example, ethylene and phenol are the main products of the conversion of ethane–benzene–N_2O feed. Small amounts (about 10%) of alkylbenzenes and alkylphenols are also found indicating possible alkylation of C_6H_6 and C_6H_5OH with ethylene; no significant changes are observed for the selectivity to deep oxidation products. The similar composition of the products for conversion of individual and binary hydrocarbon feeds means that the first step of the reaction, namely interaction of α-oxygen with the reactants, is the same for these two cases and, therefore, the amount of reactant converted reflects the relative reactivity.

To calculate quantitatively the relative reactivity let us assume the following reaction scheme for a binary feed (e.g., methane and ethane) where reactants compete for active oxygen formed from N_2O:

$$\begin{aligned} &[\ ] + N_2O \longrightarrow [\mathrm{O}] + N_2,\\ &[\mathrm{O}] + CH_4 \xrightarrow{k_{CH_4}} [\ ] + P_1,\\ &[\mathrm{O}] + C_2H_6 \xrightarrow{k_{C_2H_6}} [\ ] + P_2 \end{aligned} \tag{1}$$

where [ ] denotes site of N_2O decomposition (reduced surface site), [O] is α-oxygen (oxidised surface site), P_1 and P_2 are products, and k_{CH_4} and $k_{C_2H_6}$ are rate constants of interaction of α-oxygen with hydrocarbons.

For this scheme the rates of CH_4 and C_2H_6 conversion can be expressed as

$$\begin{aligned} \frac{\mathrm{d}P_{CH_4}}{\mathrm{d}\tau} &= -k_{CH_4} P_{CH_4} \theta_{\mathrm{ZO}},\\ \frac{\mathrm{d}P_{C_2H_6}}{\mathrm{d}\tau} &= -k_{C_2H_6} P_{C_2H_6} \theta_{\mathrm{ZO}}. \end{aligned} \tag{2}$$

The system is valid, if (i) there are no other routes for hydrocarbon conversion (it seems quite probable taking into account about 100% selectivity), and (ii) hydrocarbons react with α-oxygen from the gas phase. The modification of the system (2) with subsequent integration gives equation (3), where $P_{CH_4}, P_{C_2H_6}, P^0_{CH_4}$ and $P^0_{C_2H_6}$ are current and initial partial pressures of methane and ethane:

$$\ln\left(\frac{P_{CH_4}}{P^0_{CH_4}}\right) = \frac{k_{CH_4}}{k_{C_2H_6}} \ln\left(\frac{P_{C_2H_6}}{P^0_{C_2H_6}}\right). \tag{3}$$

It is evident from (3) that the plot of $\ln(P_{CH_4}/P^0_{CH_4})$ versus $\ln(P_{C_2H_6}/P^0_{C_2H_6})$ must be a straight line with a slope equal to $k_{CH_4}/k_{C_2H_6}$ and this ratio can be accepted as a measure of relative reactivity of hydrocarbons. It is important to emphasise that the relative reactivity, calculated in such a way, does not depend on the possible parallel reactions of surface oxygen with other hydrocarbons present in the reaction mixture or on secondary conversion of the primary products. Moreover, the equation does not contain partial pressure of the oxidant (the coverage of active surface oxygen species [O] or the number of active sites), therefore, the ratio of the kinetic constants can be calculated independently of the N_2O conversion. As far as the selectivities of hydrocarbon conversions are constant, the values of rate constant ratios seem also not to depend on the degree of catalyst deactivation.

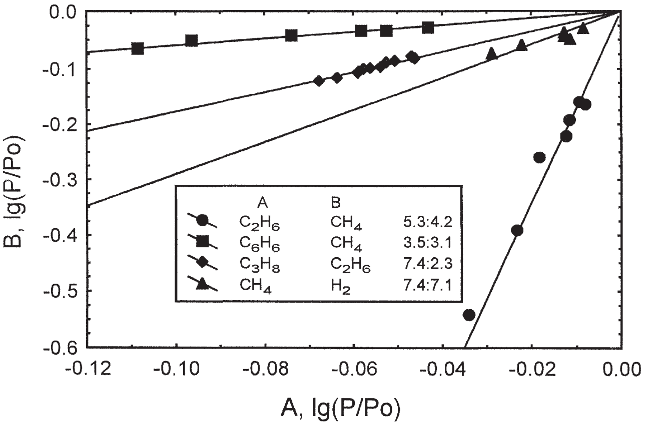

Figure 1. Plot for determination of relative reactivities according to equation (3). $T = 418\,^{\circ}\mathrm{C}$, initial feed compositions are given on the plot (vol%), $C_{\mathrm{N_2O}} = 8$–10 vol%, helium balance.

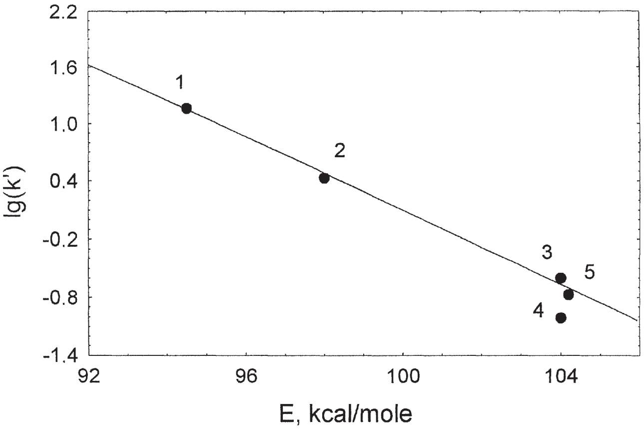

Figure 2. Variation of the relative rate constants k'_{rel} corrected for the number of C–H bonds as a function of C–H bond energy: 1 – propane, 2 – ethane, 3 – methane, 4 – benzene, 5 – hydrogen.

Figure 1 shows the experimental data for conversion of binary mixtures plotted in on corresponding coordinates. It is evident from figure 1 that for all combinations studied linear correlations are observed, the data for fresh and deactivated catalysts satisfying the same straight lines. From the slope of the plots relative reactivities $k_{\mathrm{r},i} = k_i/k_{\mathrm{CH_4}}$ are estimated, where methane is taken as a standard substance. Calculated values of relative rate constants are summarised in table 2, together with confidence intervals for 95% probability. As could be expected, propane and ethane are the most reactive substances; the reactivities of hydrogen and methane are found to be almost the same. An unexpected result of the experiments is that benzene is found to be as reactive as CH_4 and H_2.

A very high (about 100%) selectivity to principal products (ethylene from ethane, propylene from propane and phenol from benzene) indicates that under the experimental conditions used active oxygen attacks only a C–H bond of the hydrocarbon molecule (H–H for hydrogen), therefore, the properties of the C–H bond can influence the course of the reaction, to our mind, the most important factor being strength of the bond.

The values for C–H bond strengths listed in table 2 are taken from [9]. A value 94.5 kcal/mol is used for propane which corresponds to the sec-H–$CH(CH_3)_2$ bond. It is clear from table 2 that an increase in strength of C–H bond E correlated with a substantial decrease of the relative rate constant k_{rel} (correlation coefficient $r = 0.96$). If it is the value of E that determines the rate of conversion then the rate of overall conversion is determined by the weakest C–H bond of the molecule and one can estimate the relative reactivity of the single C–H bond towards α-oxygen as

$$k'_{\mathrm{rel}} = k_{\mathrm{rel}}/N, \tag{4}$$

where k_{rel} is relative rate constant and N number of the weakest equivalent C–H bond in the molecule.

Table 2
Relative rate constants (k_{rel}), energy of C–H bonds ($E_{\mathrm{C–H}}$) and number of equivalent protons (N_{H}) for the studied compounds.

Reactant	k_{rel}	$E_{\mathrm{C–H}}$ (kcal/mol)	N_{H}
CH_4	1.000	104.0	4
C_2H_6	16.2 ± 1.2	98.0	6
C_3H_8	28.9 ± 2.3	94.5	2
C_6H_6	0.583 ± 0.047	104.0	6
H_2	0.335 ± 0.067	104.2	2

These values of k'_{rel} constants (corrected for the number of equivalent C–H bonds) are plotted in figure 2. An excellent correlation (correlation coefficient $r > 0.99$, point for benzene is excluded) between E and k'_{rel} for methane, ethane, propane and hydrogen strongly supports the assumption that it is the C–H bond strength that determines the rate of hydrocarbon conversion. Moreover, we can conclude that the intermediate states of reaction of surface oxygen with the alkane (hydrogen) are also similar and it is no necessity in any additional activation of hydrocarbon (for example on acid sites).

The greatest difference between regression line and experimental data is found for benzene, for which the value of k'_{rel} is less than that expected from the strength of the C–H bonds. It was shown earlier [10] that the value of kinetic isotope effect (KIE) for oxidation of methane with α-oxygen ranges from 1.9 to 5.5 at temperatures from -50 to $100\,^{\circ}\mathrm{C}$ while no KIE was found for benzene. These data were interpreted as a rate-limiting C–H bond cleavage in the case of CH_4, whereas oxidation of C_6H_6 is limited by the interaction of α-oxygen with a C=C bond giving an epoxy-type intermediate [10]. In our case the deviation of k'_{rel} for benzene from the regression line for alkanes and H_2 (figure 2) is hardly reflected by the distinction of reaction mechanisms. Taking into account the values of self-diffusion coefficients for benzene (from 10^{-11} to 2×10^{-12} cm^2 s^{-1}, $77\,^{\circ}\mathrm{C}$ [11]), methane and propane (1×10^{-4} and 5×10^{-5} cm^2 s^{-1}, $27\,^{\circ}\mathrm{C}$ [12]), the most probable explanation of the lesser reactivity of benzene is transport limitation that decreases the actual concentration of C_6H_6 in the vicinity of active centres inside the zeolite channels.

It should be pointed out that despite all substances studied satisfy the common dependence in respect to interaction with α-oxygen (with some deviation for benzene), the subsequent transformation of the [O–hydrocarbon] complex depends on the type of reactant used and leads to: (i) deep oxidation products (for CH_4), (ii) products of dehydrogenation (for C_2H_6 and C_3H_8,) or (iii) hydroxylated substances (for C_6H_6). On the basis of data presented, there is no possibility to define the factors which determine the subsequent transformation of the surface [O–hydrocarbon] complex, but it is no doubt that key factor for reactivity of hydrocarbons is the energy of the attacked C–H bond.

4. Conclusion

Formation of active surface oxygen species is crucial for hydrocarbon conversion on ZSM-5 in the presence of N_2O; there is no necessity for additional activation of hydrocarbons, such as on acid sites. The relative reactivity of hydrocarbons towards interaction with α-oxygen is determined by the strength of the attacked C–H bond.

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