ELSEVIER

Catalysis Today 61 (2000) 129–136

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Chemistry of surface oxygen formed from N_2O on ZSM-5 at moderate temperatures

S.N. Vereshchagin [a,*], N.P. Kirik [a], N.N. Shishkina [a], S.V. Morozov [b], A.I. Vyalkov [b], A.G. Anshits [a]

[a] *Institute of Chemistry and Chemical Engineering SB RAS, K.Marx 42, Krasnoyarsk 660049, Russia*
[b] *Institute of Organic Chemistry SB RAS, Prosp. Akad. Lavrentieva 9, Novosibirsk 630090, Russia*

Abstract

Conversion of CH_4, C_2H_6, C_3H_8, benzene and their binary mixtures over H-NaZSM-5 catalyst in the presence of N_2O was studied. It was found that under experimental conditions methane alkylates benzene to give toluene and xylenes. Acidity of the catalyst had no effect on the reactivity of active oxygen formed from N_2O towards methane and benzene, but affected their secondary transformation. Acidic samples favored the reaction of aromatic ring methylation with methane whereas deep oxidation of CH_4 prevailed on NaHZSM-5. Based on the relative reactivities and ^{13}C label distribution in the products of $^{13}CH_4+C_6H_6+N_2O$ feed conversion, the scheme of hydrocarbon transformation was proposed.

Keywords: Hydrocarbon; Zeolite; N_2O; ZSM-5

1. Introduction

Hydrocarbon conversion over ZSM-5 zeolites (or iron-ZSM-5 analogs) in the presence of N_2O is a promising subject of studies because of the peculiar properties of active surface oxygen species formed from N_2O which have been called as α-oxygen. Extensive studies of chemical properties of α-oxygen have been undertaken at ambient temperature [1], but there are only limited data available concerning the chemistry of α-oxygen at temperatures of catalytic processes. It is known that the system N_2O-ZSM-5 is capable of converting methane to the mixture of aromatic hydrocarbons [2], selectively dehydrogenates ethane to ethylene at T=360–420°C [3] and hydroxylates aromatic ring of benzene and its derivatives with up to 96–98% selectivity [1,4]. A number of recent papers consider the system N_2O-ZSM-5(or Fe-ZSM-5)-hydrocarbon for the removal of N_2O from waste gases [5]. Though the process of benzene to phenol hydroxylation with N_2O was demonstrated by Solutia on a pilot plant scale, we are still far from understanding the reaction mechanism. But it is evident that the knowledge of regularities of α-oxygen formation and its interaction with different hydrocarbons could be very useful for understanding the general concept of selective conversion of low alkanes and for the design of active catalysts. The objective of the present paper is to study the peculiarities of hydrocarbon transformation in the presence of N_2O under conditions of catalytic reaction as a part of the chemistry of the oxygen species produced on the surface of ZSM-5 from nitrous oxide.

* Corresponding author. Fax: +7-3912-439431.
E-mail address: snv@krsk.infotel.ru (S.N. Vereshchagin).

0920-5861/00/$ – see front matter
PII: S0920-5861(00)00355-2

2. Experimental

Starting sample of zeolite HZSM-5 (SiO_2/Al_2O_3= 33, the contents of sodium <0.01 wt.%, iron 0.06 wt.%) was prepared from NaZSM-5 by triple ion exchange with 1 M NH_4Cl followed by calcination at 550°C in air. HZSM-5 was then impregnated at room temperature with 2–5 N NaOH solution (about 0.2 ml/(g zeolite) to reach desired content of sodium, dried at 40°C and calcined at 550°C in oxygen flow prior to catalysis. No loss of zeolite crystallinity was found for Na-containing samples according to XRD. Catalytic runs were carried out at atmospheric pressure and 350–450°C in a conventional setup with stationary catalyst bed. Feed composition: RH/N_2O from $\frac{5}{1}$ to $\frac{1}{3}$ (where RH — methane, ethane, propane, benzene, hydrogen or their binary mixtures). Analyses of the reactants and reaction products were carried out using on-line gas chromatograph equipped with packed and capillary columns. Gases coming out of the reactor were additionally bubbled through liquid hexane or CCl_4 kept at 0°C to absorb C_6^+ products; these solutions were used for GC–MS and NMR analyses.

Rates of hydrocarbon conversion and relative reactivity were calculated from the conversion of the feed of two hydrocarbons and N_2O as described elsewhere [6]. GC–MS analyses of the liquid products of $^{13}CH_4+C_6H_6+N_2O$ conversion were performed on HP 6890A chromatograph equipped with MSD 5972A and 30 m capillary column HP-5MS (5% phenyl methyl siloxane). NIST mass spectral database and retention times of reference compounds were used to identify unknown substances. ^{13}C isotope distribution and location of labeled atoms were calculated from mass spectra (GC–MS data) and from ^1H and ^{13}C NMR spectra.

3. Results and discussion

3.1. Relative reactivities of hydrocarbons

In accordance with the published data [1,2], catalytic conversion of methane, ethane (propane) and benzene in the presence of N_2O on ZSM-5 leads to different types of products, which are summarized in Table 1. Whereas methane undergoes basically deep oxidation to CO_2 and CO with a small amount of aromatics, ethane (propane) is selectively dehydrogenated to ethylene (propylene); benzene is hydroxylated to phenol with 95–98% selectivity. The conversion of the hydrocarbons drops rapidly with time on stream (indicating deactivation of the catalyst), though the selectivity remains almost constant, the rate of activity decrease being different for different hydrocarbon feeds (from 1.5 to 4 times for the first 20 min of run).

Table 1
Principal and minor products formed on HZSM-5 type catalysts at 380–420°C from different hydrocarbons in the presence of N_2O (C_{RH}=3–15 vol.%, C_{N_2O} = 3–10 vol.%, He balance, RH conversion less than 10%)

RH	Main products (selectivity %)	Minor products
Methane	CO, CO_2 (80–95)	Aromatic hydrocarbons, ethylene
Ethane	C_2H_4 (90–98)	C_3–C_6 olefins, aromatic hydrocarbons, CO_2, CO
Propane	C_3H_6 (90–98)	C_4–C_6 olefins, aromatic hydrocarbons, CO_2, CO
Benzene	C_6H_5OH (>95)	CO_2, CO

These observed directions of hydrocarbon conversion can be connected either with mechanism of hydrocarbon interaction with surface oxygen or with subsequent conversion of activated species. To understand this catalytic behavior we have studied the reactivity of hydrocarbons towards surface oxygen formed from N_2O. It is very difficult to compare absolute reactivities (kinetic constants of reactions (1, 2)) because of unknown kinetic equation and different rates of deactivation, but relative reactivities, expressed as $k_{rel} = k_{RH}/k_{CH_4}$ can be calculated from the conversion of binary hydrocarbon feed RH–CH_4–N_2O–He. According to Eq. (3), which is derived from integration of kinetic equation for (1) and (2), the value of k_{rel} is equal to the slope of a straight line in coordinates $\ln(P_{RH}/P^0_{RH}) - \ln(P_{CH_4}/P^0_{CH_4})$, where $P^0_{CH_4}$, P^0_{RH}, P_{CH_4}, P_{RH} are the partial pressures of methane and RH before and after reactor, respectively [6].

$$CH_4 + [O] \xrightarrow{k_{CH_4}} \text{products} \quad (1)$$

$$RH + [O] \xrightarrow{k_{RH}} \text{products}, \quad \text{where } RH = C_3H_3, C_2H_6, H_2 \text{ or } C_6H_6 \quad (2)$$

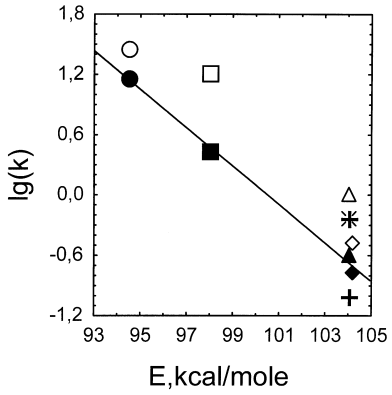


Fig. 1. Variation of k_{rel} (open symbols) and k'_{rel} (closed symbols) as a function of energy of C–H bond E; propane (○, ●), ethane (□, ■) methane(△, ▲), hydrogen (◇, ◆) and benzene (∗, +).

$$\ln\left(\frac{P_{CH_4}}{P^0_{CH_4}}\right) = \frac{k_{CH_4}}{k_{RH}} \ln\left(\frac{P_{RH}}{P^0_{RH}}\right) \quad (3)$$

$$k'_{rel} = \frac{k_{rel}}{N} \quad (4)$$

The values of k_{rel}, calculated in such a way, decrease in the order C_3H_8>C_2H_6>CH_4≈H_2≈C_6H_6. High selectivity to principal products (Table 1) indicates that α-oxygen attacks only C–H bond of hydrocarbon molecule (H–H for hydrogen), therefore, the properties of C–H bond can influence the course of the reaction. Fig. 1 (open symbols) shows the variation of k_{rel} as a function of energy of C–H bond E (the weakest sec-H–C bond for C_3H_8 is considered). 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 the relative reactivity of the single C–H bond towards α-oxygen can be estimated as (4), where k_{rel} is the relative rate constant and N the number of the weakest equivalent C–H bond in molecule. An excellent linear correlation between energy of C–H bond and corrected relative reactivity k'_{rel} (Fig. 1, closed symbols) indicates that it is the strength of C–H bond (H–H for hydrogen) that determines the rate of alkanes conversion.

The reactivity of benzene is found to be close to that of methane and fits in with the correlation line for alkanes though the value of $k'_{C_6H_6}$ is slightly less than predicted. The data presented do not allow to distinguish between C–H bond and C=C bond attack for hydroxylation of C_6H_6. A reaction mechanism which includes C=C double bond attack has been proposed earlier [7]. Based on the values of kinetic isotope effect (KIE) for oxidation of methane (KIE from 1.9 to 5.5) and benzene (no KIE) with α-oxygen at temperatures −50 to +100°C, it was postulated that a rate limiting C–H bond cleavage occurs in the case of CH_4, whereas oxidation of C_6H_6 is limited by the interaction of α-oxygen with C=C bond giving an epoxy-type intermediate [7]. It is necessary to note that one should be very careful applying results obtained at ambient (or sub-ambient) temperature to catalytic region. At low temperatures the peculiarities of the catalytic behavior can be attributed to extremely different mobility of the hydrocarbons studied, taking into account the values of self-diffusion coefficients for benzene (1×10^{-11} to 2×10^{-12} $cm^2\ s^{-1}$, 77°C [8]), methane and propane (1×10^{-4} and 5×10^{-5} $cm^2\ s^{-1}$, 27°C [9]). In our case the low reactivity of benzene can be explained not only by the distinction of reaction mechanisms but also by transport limitation that decreases the actual concentration of C_6H_6 in the vicinity of active centers inside the zeolite channels.

As the values of adsorption coefficients for methane and benzene are very different it is interesting to elucidate the influence of acidity on the reactivity of these two the most inactive organic substances. TPD profiles of ammonia for the zeolites with different amount of strong acid sites are shown on Fig. 2a; Fig. 2b shows the plot which allows to determine the relative reactivity of CH_4–C_6H_6 pair according to (3) for these samples. It is evident that within experimental error all data satisfy the same linear dependence indicating that the relative reactivity of methane and benzene does not depend on acidity. Therefore one can conclude that the first step of the transformation is the interaction of surface oxygen species with the molecule of hydrocarbon and there is no additional activation on acidic site.

3.2. Peculiarities of CH_4–C_6H_6–N_2O feed conversion — benzene methylation with methane

A remarkable feature of CH_4–C_6H_6–N_2O conversion over HZSM-5 is the absence of CO_2, CO and enhanced amount of toluene (Tol) and diphenylmethane (DPhM) compared with that for streams of methane and benzene (Table 2). Xylenes (Xy), cresols (Cre),

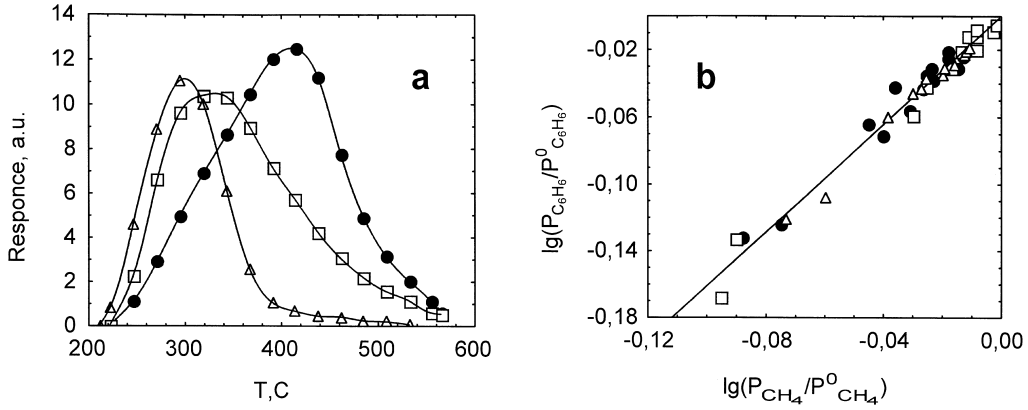


Fig. 2. (a) NH_3 TPD profile (T_{ads}=200°C, β=10° min^{-1}) and (b) relative reactivity of methane and benzene for: (●) HZSM-5; (□) 1.5% NaHZSM-5; (Δ) 2.5% NaZSM-5.

indene (Ind), naphthalene (Naph) and methylnaphthalene are also formed in minor amounts (Fig. 3). Three different reaction pathways can be proposed to explain this observation: (i) alkylated aromatics are formed from methane, benzene blocks the process of deep oxidation of activated CH_4; (ii) alkylated aromatics originate from the process of benzene self-alkylation which is known to occur over acidic zeolites [10,11] or (iii) methane alkylates aromatic ring of benzene; in this case C_6H_6 intercepts surface species formed from CH_4, preventing from deep oxidation.

To clarify the origin of methylated compounds a special experiment was carried out in which ^{13}C labeled methane (72% of $^{13}CH_4$) and benzene with natural ^{13}C content (1.1%) were converted over ZSM-5 catalysts in the presence of N_2O and liquid products were subjected to GC–MS, ^1H and ^{13}C NMR analyses. If the pathway (i) takes place then content of ^{13}C in aromatics must be equal to that for $^{13}CH_4$ (72%); no addition of ^{13}C to products is expected for the route (ii) and only methyl group will contain isotope for the route (iii).

Table 2
Amount of liquid products formed on HZSM-5 at 418°C with different reaction feeds. Time of stream 2000 s, GHSV=26 500 h^{-1}

Reaction feed (vol.%, He balance)			
CH_4	14	14	–
C_6H_6	3.5	–	3.5
N_2O	5.7	5.8	5.8
Amount of products (mmol g^{-1})			
Tol	0.58	0.049	–
Xy	0.036	0.063	–
Phenol	0.63	0.004	0.6
Ind	0.08	0.014	–
Cre	0.23	0.008	–
DPhM	0.19	–	–

The number of labeled atom in a molecule can be easily calculated from the position of molecular ion in the mass spectrum. Fig. 4 shows Tol mass spectra for reaction of CH_4–C_6H_6–N_2O and $^{13}CH_4$–C_6H_6–N_2O over HZSM-5. The group of peaks at m/z=92 (molecular ion of Tol, Fig. 4a) is evidently increased by unity of m/z in the case of $^{13}CH_4$ conversion (Fig. 4b). Slightly different appearance of molecular ion peaks for labeled and not labeled Tol (Fig. 4) arises from 72% enrichment of methane with ^{13}C, which makes possible to form Tol with 0, 1 or 2 ^{13}C atoms. The increase of molecular ion position by one m/z is observed also for Cre (m/z=106) and DPhM (m/z=168) and points to the presence of only one ^{13}C atom in the molecules of Tol, Cre and DPhM.

Similar analysis of the mass spectra of Xy (m/z=108) reveals that two atoms of ^{13}C label are present in their molecules. Therefore the number of ^{13}C label in the molecules of Tol, Cre and Xy is equal to the number of methyl groups. It is not possible to determine the exact position of the label on the basis of mass spectrum because of the scrambling of the carbon atoms after ionization, but ^{13}C NMR spectra of the liquid products display that the label is located

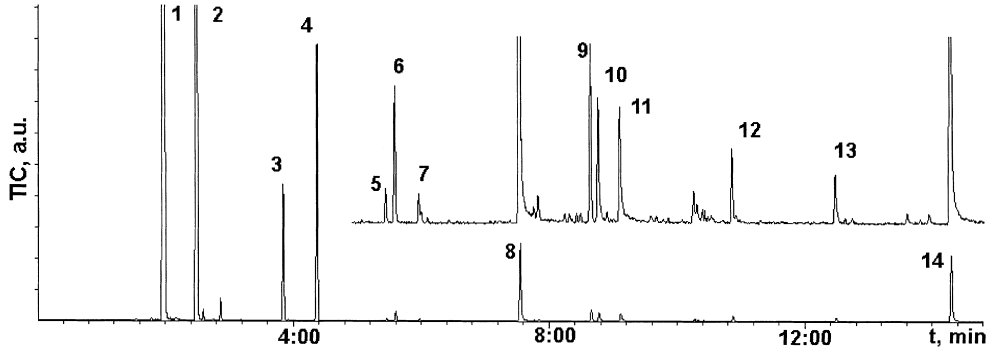


Fig. 3. GC–MS profile of liquid products of methane–benzene transformation on 1.5% NaHZSM-5, feed composition (vol.%): CH_4 14%, C_6H_6 3.5%, N_2O 3%, He balance. T=418°C, GHSV=26 500 h^{-1}, reaction time 2000 s. 1-hexane (solvent), 2-benzene, 3-Tol, 4-*n*-octane (internal standard), 5-ethylbenzene, 6-*m*+*p* Xy, 7-*o*-Xy, 8-phenol, 9-Ind, 10,11-Cre, 12-Naph, 13-2-methylnaphtalene, 14-DphM.

presumably in methyl groups of Tol (δ=21.38 ppm), Xy (δ=21.25, 20.97 ppm) and CH_2-group of DPhM (δ=41.82 ppm). The isotope enrichment of methyl group of Tol calculated from GC–MS (71% ^{13}C) is in good agreement with initial content of ^{13}C in methane (72%). No mass-spectroscopy or ^{13}C NMR data show any insertion of carbon label in the aromatic ring of phenol. Therefore, under experimental conditions employed Tol and Xy are formed via methylation of aromatic ring with methane; CH_3 groups of Cre and CH_2 group of DPhM also originate from CH_4. It is reasonable to suggest that DPhM is formed from Tol and benzene, the mechanism being similar to that for methane.

Side chain oxidative methylation of aromatic substances was shown to occur for high temperature homogeneous non-catalytic conversion of Tol–methane–oxygen mixtures at 700–750°C and was accompanied by reactions of deep oxidation and cracking [12]. In the case of HZSM-5 addition of methyl group to aromatic ring occurs at relatively low temperature and no CO_2 formation is observed.

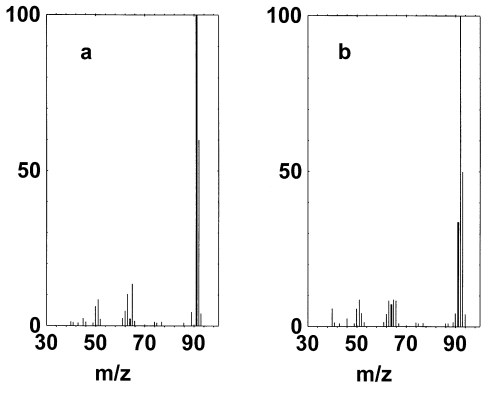


Fig. 4. Tol mass spectra for reaction of (a) CH_4–C_6H_6–N_2O and (b) $^{13}CH_4$–C_6H_6–N_2O over HZSM-5 at 418°C.

Composition of the products obtained over 2.5% NaZSM-5 differs from that over HZSM-5. For acidic sample the formation rates of phenol and Tol are about equal (Table 2), but for non-acidic zeolite the rate of Tol formation is more than an order of magnitude lower (Fig. 5a) and only traces of aromatic compounds are found. The conversion of methane remains the same but CO_2, CO and coke are predominantly formed instead of methylated aromatic compounds. Intermediate activity of Tol and CO_2 formation is found for 1.5% NaHZSM-5. It is necessary to emphasize that the total activity and the rate of phenol formation are comparable for these three catalysts (Fig. 5b), acidity changes cause only the decrease of the yield of alkylated aromatics and increase the CO_2 formation.

3.3. Scheme of hydrocarbon transformation

The following reaction sequence for alkylated aromatics formation can be deduced from the reported data (Scheme 1). Methane reacts with surface α-oxygen to give active hydrocarbon species $[CH_4 \cdots O]$ which can be further oxidized by excess of oxidant to CO and CO_2. It can lose some hydrogen via either oxidative dehydrogenation or hydrogen redistribution and forms coke precursor. Additional

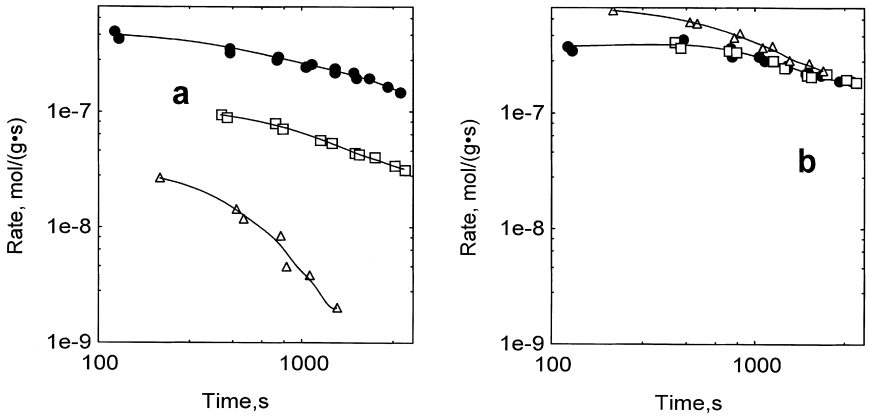
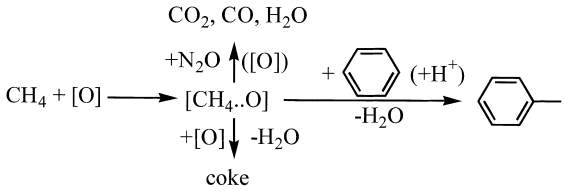


Fig. 5. Rate of Tol (a) and phenol (b) formation as a function of time of stream. (●) HZSM-5; (□) 1.5% HNaZSM-5; (Δ) 2.5% NaZSM-5.

route exists on acidic zeolites — methylation of low molecular weight reagents (benzene, Tol) releasing Tol and Xy to the gas phase.

The key point of the scheme is the nature of hydrocarbon–[O] complex and the factors which determine subsequent transformation. According to the reactivity of the hydrocarbons the first stage of the reaction is the interaction of α-oxygen with C–H bond, this step being similar for all alkanes studied. As it was shown [1] the interaction of α-oxygen with methane at ambient temperature leads to the formation of methanol which can be removed from the surface with appropriate solvent. In our case we do not observe methanol in the products of catalytic conversion of CH_4–N_2O or CH_4–C_6H_6–N_2O feed for any of the zeolite samples studied. Of course the absence of CH_3OH may be attributed to conversion over acid sites or decomposition to $CO+H_2$ over non-acidic 2.5% NaZSM-5. Very low H_2/CO ratio (about $\frac{3}{26}$) found for CH_4–N_2O feed [13] makes this assumption doubtful. To our mind the RH–[O] complex which leads to alcohols at ambient temperature



Scheme 1.

is rather unstable at temperatures of catalysis. One of the possible route of its transformation is decomposition (reactions 5). The radicals $CH_3^\bullet$ and $C_2H_5^\bullet$ are released to the gas phase and coupled to give ethane and *n*-butane which have been shown to observed for C_2H_6–N_2O conversion over NaHZSM-5 [13].

$$[CH_4 \cdots O] \rightarrow CH_3^\bullet + {}^\bullet OH_s \quad \text{or}$$
$$[C_2H_6 \cdots O] \rightarrow C_2H_5^\bullet + {}^\bullet OH_s \qquad (5)$$

Another route for RH–[O] transformation can be proposed if we assume that α-oxygen tends to withdraw two hydrogen atoms from the reactant molecule to form H_2O. The progress of the reaction in this case depends on whether hydrocarbon can supply two H atoms. Ethane or propane can easily uncouple two hydrogen atoms giving olefins and water and releasing the active site according to reaction (6). The process of removal of two hydrogen from benzene is very improbable because of steric hindrances and stability of aromatic ring structure, the corresponding complex is relatively stable and its transformation results in C–H bond oxygen insertion, giving phenol (7). Unlike benzene, methane does not form stable complex and is capable to provide two hydrogen atoms. The implied resulting species carbene ($:CH_2$) is known to be very active and is expected to undergo fast transformation. Intermediate carbene formation have been already proposed for methanol-to-hydrocarbon conversion over HZSM-5 [14]. The indication that carbene is formed under the condition of hydrocarbon–N_2O transformation is described in [15] where trace forma-

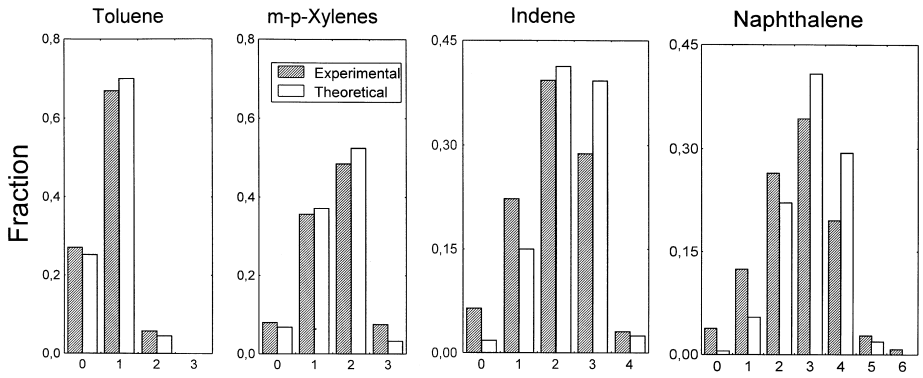


Fig. 6. Theoretical and experimental distributions of number of ^{13}C atoms in hydrocarbon molecules obtained over HZSM-5 for $^{13}CH_4$–C_6H_6–N_2O. Reaction conditions see in Table 2.

tion of cyclopropane was observed for conversion of CH_4–ethylene–N_2O feed over NaHZSM-5 (ethylene was used as a trap for $:CH_2$). If there is no acid sites on the surface $[CH_4 \cdots O]$ is quickly oxidized with excess of oxidants or reacts with surface hydrocarbon residue. On acidic surfaces addition of proton H^+ can change the course of reaction according to Eq. (8). The newly formed ZCH_3 group can act as a methylating agent in reactions of aromatic ring methylation.

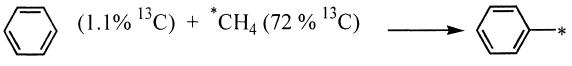
$$[C_2H_6 \cdots O] \rightarrow C_2H_4 + H_2O + [..] \quad (6)$$

$$[C_6H_6 \cdots O] \rightarrow [C_6H_6OH] \rightarrow C_6H_6OH + [..] \quad (7)$$

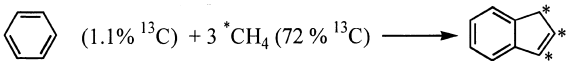
$$[CH_4 \cdots O] \rightarrow [CH_2 \cdots H_2O] + H^+Z^- \rightarrow ZCH_3 + H_2O + [..] \quad (8)$$

This mechanistic scheme is rather speculative but it can be used as a starting hypothesis for determination of structure–selectivity relationship for reaction involving α-oxygen.

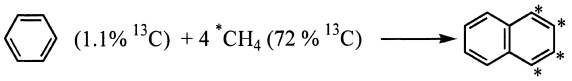
More complex reaction sequence leads to the formation of Ind, Naph and condensed aromatic hydrocarbons. Fig. 6 shows the theoretical and experimental distributions of number of ^{13}C atoms in molecules of Tol, Xy, Cre and Naph obtained over HZSM-5 for $^{13}CH_4$–C_6H_6–N_2O. Whereas for Tol and Xy theoretical and experimental distributions (calculated for the reaction (9)) are found to be very close, number of labeled carbon atoms in the molecules of Ind and Naph is found to be less than theoretically expected, according to the reactions (10) and (11).



(9)



(10)



(11)

The substantial number of non-labeled molecules and those containing only one ^{13}C atom point on the notable contribution of benzene to the formation of Ind and Naph, the reaction is accompanied with intense scrambling of ^{13}C label. Therefore condensed hydrocarbons are formed most probably by means of surface hydrocarbon's residue transformation, similar to that described for benzene self-alkylation and homologisation [10].

4. Conclusion

The rate of light alkane transformation over HZSM-5 at 418°C in the presence of N_2O (rate of interaction with α-oxygen) is determined by the strength of C–H bond of hydrocarbons. Under experimental conditions methane alkylates benzene to give

Tol and Xy. Acidic properties of the catalyst have no effect on the reactivity of α-oxygen towards methane and benzene, but acidity appears to have strong influence on the course of the secondary transformation of activated hydrocarbons. More acidic samples favor the reaction of aromatic ring methylation with methane whereas deep oxidation of CH_4 prevails on NaHZSM-5.

Acknowledgements

The authors thank V.I. Mamatyuk and M.M. Shakirov for conducting NMR experiments and spectra interpretation.

References

[1] G.I. Panov, A.K. Uriarte, M.A. Rodkin, V.I. Sobolev, Catal. Today 41 (1998) 365.
[2] S.S. Shepelev, K.G. Ione, React. Kinet. Catal. Lett. 23 (1983) 319.
[3] S.N. Vereshchagin, L.I. Baikalova, A.G. Anshits, Izv. Akad. Nauk, Ser. Khim. 8 (1988) 1718 (in Russian).
[4] M. Gubelmann, Ph. Tirel, Fr. Patent 2,630,735 (filed: May 2, 1988).
[5] C. Pophal, T. Yogo, K. Yamada, K. Segava, Appl. Catal. B 16 (1998) 177.
[6] S.N. Vereshchagin, N.P. Kirik, N.N. Shishkina, A.G. Anshits, Catal. Lett. 56 (1998) 145.
[7] K.A. Dubkov, V.I. Sobolev, E.P. Talsi, M.A. Rodkin, N.H. Watkins, A.A. Shteinman, G.I. Panov, J. Mol. Catal. A 123 (1997) 155.
[8] H. Lechert, W.D. Basler, J. Phys. Chem. Solids 50 (1989) 497.
[9] J. Kärger, Z. Phys. Chem. Leipzig 257 (1976) 983.
[10] A. Chambellan, T. Chevreau, S. Khabtou, M. Marzin, J.C. Lavalley, Zeolites 12 (1992) 306.
[11] T. Sano, et al., J. Mol. Catal. 40 (1987) 113.
[12] H.E. Hcheyan, O.M. Revenko, A.V. Borisoglebskaya, Yu.Z. Fradkov, Neftekhimia 21 (1981) 83 (in Russian).
[13] S.N. Vereshchagin, N.N. Shishkina, A.G. Anshits, Catal. Today 42 (1998) 303.
[14] C.S. Lee, M.M. Wu, J. Chem. Soc., Chem. Commun. (1985) 250.
[15] A.G. Anshits, Catal. Today 13 (1992) 495.