

Hydrocarbon conversion on ZSM-5 in the presence of N₂O: relative reactivity and routes of product formation studied by GC-MS and ¹³C NMR

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Abstract

Oxidative conversion of methane, ethane, propane, benzene, hydrogen and their binary mixtures R1–R2–N₂O–He (where R1, R2 are substances under study) were studied on HZSM-5 at 350–450°C. Relative reactivities were estimated, rate of conversion of hydrocarbons correlating with the strength of C–H bond. ¹³C label distribution in the product of ¹³CH₄–C₆H₆–N₂O feed was studied by GC-MS, ¹H and ¹³C NMR. It was shown that methane was capable to alkylate the aromatic ring under reaction condition, giving toluene and xylenes from benzene. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: ZSM-5; Alkanes; N₂O; Relative reactivity; NMR

1. Introduction

It is known that the interaction of N₂O with ZSM-5 type zeolites produces an extremely active surface oxygen species discovered by Ref. [1] which was called α-oxygen [2]. The α-oxygen is capable of converting ethane to ethylene with 96–98% selectivity; it reacts with methane at ambient temperatures to give methanol or converts benzene to phenol at moderate temperatures. To understand the origin of this extraordinary activity and selectivity, it is necessary to study both the active sites for N₂O activation (decomposition) and the details of

hydrocarbon interaction with α-oxygen. There is some information concerning the nature of N₂O activation sites and chemical properties of surface oxygen species at ambient temperatures, but there is a lack of data concerning the chemistry of α-oxygen at temperatures of catalytic processes. The objective of the present paper is to study relative reactivities of different hydrocarbons with respect to surface α-oxygen and subsequent transformations of surface species formed under condition of catalytic reaction.

2. Experimental

Starting sample of zeolite HZSM-5 (SiO₂/Al₂O₃ = 33, the contents of sodium < 0.01

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wt.%, iron 0.06 wt.%) was prepared from NaZSM-5 by ion exchange with 1 M NH_4Cl and calcined at 550°C in air. Catalytic runs were carried out at atmospheric pressure and $350\text{--}450^\circ\text{C}$ in a conventional set-up with stationary catalyst bed. Feed composition: $\text{RH}/\text{N}_2\text{O}$ from 5:1 to 1:3 (where RH = methane, ethane, propane, benzene, hydrogen or their binary mixtures). Analysis of the reactants and products formed was carried out using on-line gas chromatograph equipped with packed and capillary columns.

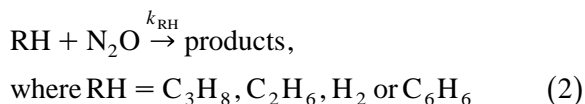
GC-MS analysis of the products of $^{13}\text{C}\text{H}_4 + \text{C}_6\text{H}_6 + \text{N}_2\text{O}$ conversion was performed on HP 6890A chromatograph equipped with MSD 5972A and $30\text{ m} \times 0.25\text{ mm}$ capillary column HP-5MS (5% phenyl methyl siloxane). ^1H and ^{13}C NMR spectra were recorded at 500.13 and 125.76 MHz, respectively, on DRX500 FT NMR spectrometer (BRUKER, Germany). All experiments were carried out without stabilization of field in 5 mm external diameter tubes. For ^1H NMR, a relaxation delay of 120 s was set. Another sample with TMS was used for calibration of field by replacement method. For ^{13}C NMR measurements, inverse-gated decoupling was used to suppress nuclear Overhauser enhancement factors; a relaxation delay of 180 s was set. Signal of solvent CCl_4 was used as internal chemical shift standard with 96.00 ppm relatively TMS. ^{13}C isotope distribution and location of labeled atoms were calculated from the GC-MS, ^1H , and ^{13}C NMR data.

3. Results and discussion

Under experimental conditions studied, the selectivity of formation of ethylene from ethane (as well as propylene from propane and phenol from benzene) is about 85–95% at conversion up to 10% and remains constant with the time though the activity decreases rapidly because of deactivation of the catalyst. Under similar conditions CO , CO_2 and coke are the main prod-

ucts of $\text{CH}_4\text{--N}_2\text{O--He}$ feeds and only 20% of methane is turned into $\text{C}_6\text{--C}_8$ aromatic hydrocarbons and ethylene.

The ratio of kinetic constants of reactions (1,2) $k_{\text{rel}} = k_{\text{RH}}/k_{\text{CH}_4}$ can be used as a relative reactivity of hydrocarbons and this ratio can be calculated from Eq. 3 for the conversion of binary hydrocarbon feed $\text{RH}:\text{CH}_4:\text{N}_2\text{O}:\text{He}$ [3].



$$\ln\left(\frac{P_{\text{CH}_4}}{P_{\text{CH}_4}^0}\right) = \frac{k_{\text{CH}_4}}{k_{\text{RH}}} \ln\left(\frac{P_{\text{RH}}}{P_{\text{RH}}^0}\right) \quad (3)$$

where P_{CH_4} , $P_{\text{C}_2\text{H}_6}$, $P_{\text{CH}_4}^0$, $P_{\text{C}_2\text{H}_6}^0$ are the current and initial partial pressures of methane and RH.

The values of k_{rel} decrease in the order $\text{C}_3\text{H}_8 > \text{C}_2\text{H}_6 > \text{CH}_4 \approx \text{H}_2 \approx \text{C}_6\text{H}_6$, benzene being found to be as reactive as CH_4 and H_2 . A linear correlation (Fig. 1) between energy of C–H bond and corrected relative reactivity $k'_r = k_{\text{rel}}/N$ (N is the number of equivalent C–H bonds) indicates that the rate of conversion can be determined by the strength of C–H bond (H–H for hydrogen).

A remarkable feature of $\text{CH}_4\text{--C}_6\text{H}_6\text{--N}_2\text{O}$ conversion over HZSM-5 is the absence of deep

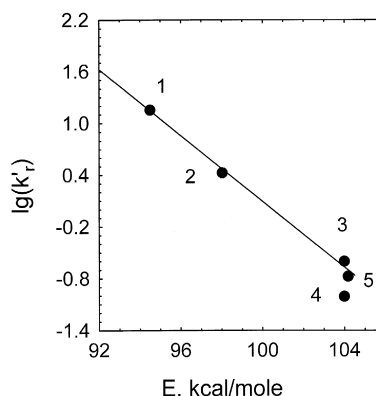


Fig. 1. Variation of the relative rate constants k'_r (corrected for the number of C–H bond) as a function of C–H bond energy: (1) propane, (2) ethane, (3) methane, (4) benzene, (5) hydrogen.

oxidation products (CO_2 , CO) and enhanced amount of toluene (Tol), xylenes (Xy), cresols

(Cre), and diphenylmethane (DPhM) (Fig. 2a) compared with that for neat methane and ben-

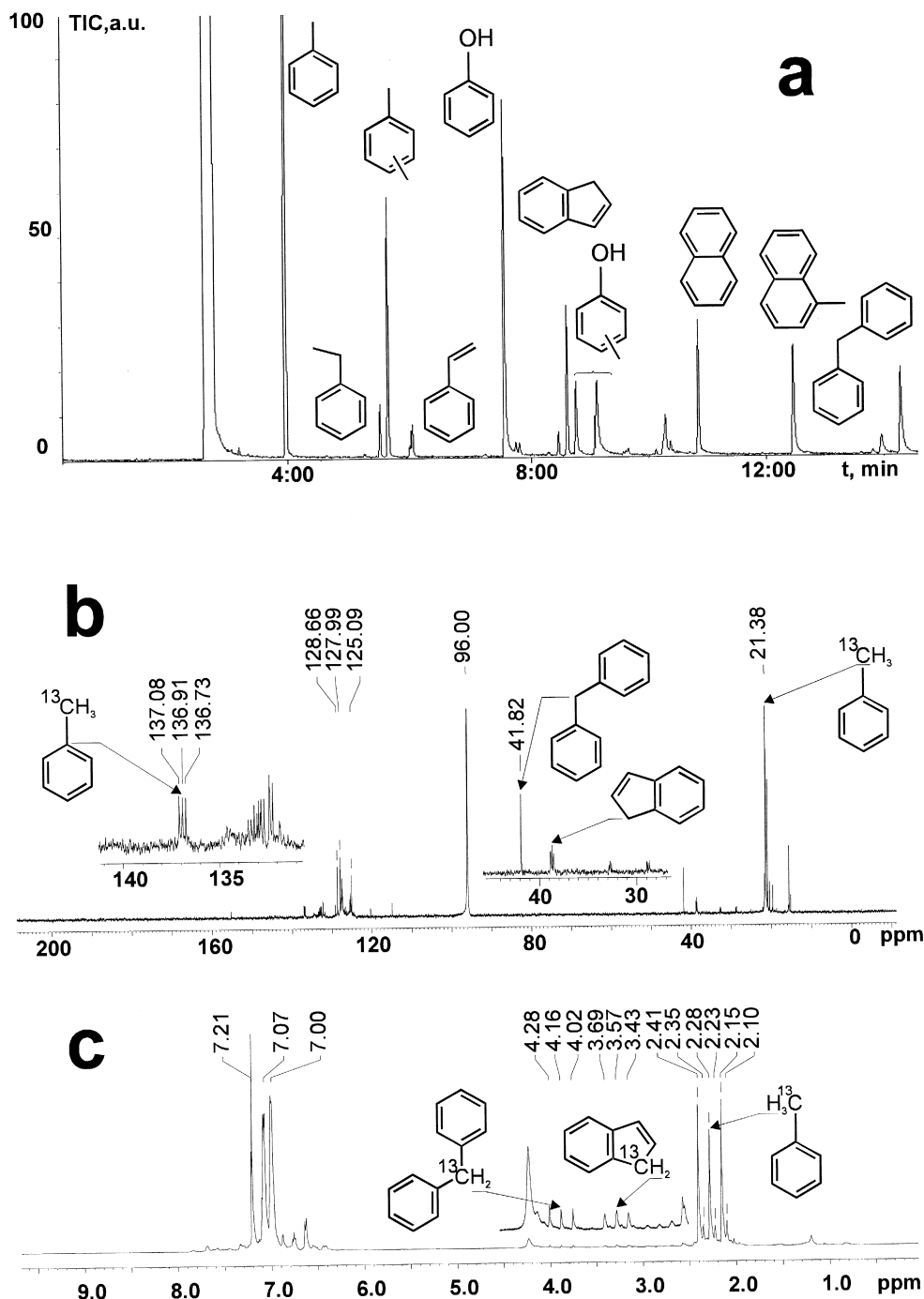
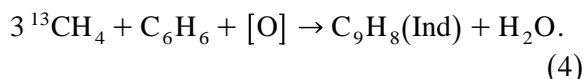


Fig. 2. (a) GC profile of liquid products of methane–benzene transformation on HZSM-5, feed composition (vol.%) $^{13}\text{CH}_4$ 13%, C_6H_6 3%, N_2O 9%, He balance. $T = 418^\circ\text{C}$, $\text{GHSV} = 5800 \text{ h}^{-1}$; (b) ^{13}C and (c) ^1H NMR spectra of liquid products of $^{13}\text{CH}_4$ – C_6H_6 – N_2O feed conversion.

zene. The conversion of labeled $^{13}\text{CH}_4\text{-C}_6\text{H}_6\text{-N}_2\text{O}$ feed have been employed to elucidate the routes of product formation. The shift of molecular ions in the mass-spectra of Tol ($m/z = 92$), Cre ($m/z = 106$) and DPhM ($m/z = 168$) corresponds to the presence of only one ^{13}C atom in the molecules. Two atoms of ^{13}C -label present in Xy ($m/z = 108$). As can be seen from ^{13}C NMR spectra (Fig. 2b), the label is located presumably in methyl groups of Tol ($\delta = 21.38$ ppm), Xy ($\delta = 21.25$ and 20.97 ppm) and CH_2 -group of DPhM ($\delta = 41.82$ ppm). The isotope enrichment of CH_3 -group of toluene calculated from GC-MS (71% ^{13}C) and ^1H NMR (71.1% ^{13}C) (Fig. 2c, $\delta = 2.41$, 2.23 and 2.15 ppm) is in good agreement with initial contents of ^{13}C in methane (72%). Neither mass-spectroscopy or ^{13}C NMR data have shown any insertion of carbon label in the aromatic ring of phenol. Therefore, for $\text{CH}_4\text{-C}_6\text{H}_6\text{-N}_2\text{O}$ feed, the main reaction route for Tol and Xy formation is the oxidative methylation of aromatic ring with methane. Benzene appears to intercept the surface species formed from methane and α -oxygen, which are converted to CO_2 in the case of $\text{CH}_4\text{-N}_2\text{O}$ feed. It is reasonable to suggest the similar reaction route for DPhM formation from toluene and benzene. More complex reaction sequence lead to formation of indene (Ind) and naphthalene (Naph). Number of labeled carbon atoms in the molecules of Ind

and Naph is found to be less than theoretically expected, according to reaction 4



Substantial number of non-labeled molecules of Ind and Naph and those containing only one ^{13}C atom show the notable contribution of benzene to their formation accompanied with intense scrambling of ^{13}C label. Therefore, condensed hydrocarbons are formed most probably by means of surface hydrocarbon's residue transformation, but detailed mechanism of the reaction needs further studies.

4. Conclusion

The reactivity of hydrocarbons in the oxidative conversions on HZSM-5 in the presence of N_2O has been found to correlate with the strength of C–H bond. Under reaction condition, methane is able to alkylate the aromatic ring of benzene giving toluene and xylenes.

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