On the formation of C_3 hydrocarbons during the conversion of ethanol using H-ZSM-5 catalyst

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The formation of predominating C_3 species during the conversion of ethanol on H-ZSM-5 catalyst was examined as a function of temperature, time on stream and space velocity. The trends observed indicated that propene was formed from the cracking of larger olefins, possibly 4-methylpentene, and not as an intermediate between C_2 and C_4 production. The parallel formation of propene with naphthenes and aromatics resulted in significant hydrogen-transfer activity leading to propane, while ethylene and butenes played a much less significant role in the process.

Keywords: conversion; ethanol; H-ZSM-5; propane formation; propene formation

1. Introduction

The conversion of ethanol to hydrocarbons using H-ZSM-5 zeolite catalyst offers an alternative and renewable source of gasoline, olefins, and aromatics to their production from crude oil cracking [1–12]. In order to optimize the ethanol conversion process for any particular range of hydrocarbons, details of the reaction pathways are critical. These pathways have been assumed to be similar to those of the well known analogous methanol-to-gasoline (MTG) process, so that ethanol is first converted to diethylether and subsequently to ethylene [1]. Through the polymerization of ethylene or its condensation with additional molecules of ethanol, higher olefins are formed which eventually cyclize and aromatize. With ethanol, however, the starting unit is an even carbon number species and it is therefore interesting that C_3 hydrocarbon species predominate in the gaseous fraction of the conversion products whilst amongst the liquid product (C_{5+}) also, many odd carbon number hydrocarbons, mainly toluene, are formed in significant concentra-

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tions [11,12]. The stage at which C_3 species are formed during the process may play a pivotal role in the final composition of the gaseous product as well as the composition of the liquid product. In this paper we examine the production of these C_3 species during the conversion of ethanol.

2. Experimental

2.1. SYNTHESIS OF H-ZSM-5

ZSM-5 was prepared by combining 49.8 g of sodium silicate (Aldrich, 27% SiO_2, 14% NaOH) and 86.0 g of deionized water to which was added 6.7 g of tetrapropylammonium bromide (Aldrich, 98%) dissolved in 17 g of water with stirring. 2.27 g of aluminum sulfate (BDH, AR) dissolved in 17 g of water and 4.1 g of concentrated sulphuric acid (BDH, AR) was then added to the stirred reaction mixture and the resulting gel was placed in a 150 cm^3 PTFE-lined, screw cap, stainless steel autoclave and allowed to crystallize hydrothermally in an oven under autogeneous pressure and static conditions at 120°C for 24 h, followed by 170°C for 30 h. The solid product was then recovered by filtration, washed with deionized water, air dried, then oven dried at 110°C. The ZSM-5 sample was calcined in a flowing stream of air at 550°C for 24 h in a furnace, then converted to the H-form by stirring in dilute HCl (0.5 M, 23 cm^3/g) at 80°C for 16 h. Samples were recovered by filtration, washed free of chloride, air dried, then oven dried at 110°C. Chemical analysis was done on the calcined, H-form of the zeolite. The sodium content was determined by flame photometry, silicon and water content by gravimetric analysis and aluminum by neutron activation analysis. The "as-synthesized" and calcined samples were characterized by X-ray diffraction using a Siemens D5000 Fourier transform diffractometer equipped with monochromators, Cu Kα radiation and nickel filters. The morphologies and crystal sizes of the zeolite sample were determined using a Jeol T200 scanning electron microscope. The IR spectra of the sample were recorded as KBr disc using a Perkin Elmer 1710 Fourier transform infrared spectrometer and the intensity ratio of the 450 and 550 cm^{-1} IR bands was used to determine crystallinity as described in the literature [13,15]. The local environment of Al in the sample was determined by solid state ^{27}Al MAS NMR using a Bruker MSL-400 instrument. The chemical composition of the sample was determined to be $Na_{0.07}H_{4.09}Al_{4.16}Si_{91.8}O_{192}\cdot 19H_2O$ with Si/Al ratio of 22.1 and 98.8% proton exchanged. Characteristic peaks of 2θ versus relative intensity, as well as low background in the XRD pattern showed the sample to be highly crystalline ZSM-5. From the IR spectrum an optical density ratio of (i.e. the 450/550 cm^{-1} bands in the IR spectrum) > 0.8 was calculated, thereby also indicating a high crystallinity. A single sharp signal at 56.8 ppm in the ^{27}Al NMR spectrum indicated that the aluminum present were in tetrahedral coordination. Scanning electron micrographs showed the sample to be composed of agglomerates (< 2 μm) of microcrystalline particles.

2.2. CATALYTIC STUDIES

Ethanol conversion was performed at atmospheric pressure using a vertically mounted, continuous flow, pyrex reactor (20 cm × 1.5 cm). The reactor tube was placed in a surrounding tube furnace which was heated by nichrome wire. For each run, 1.0 g of the catalyst was supported in the center of the reactor tube on a glass frit and conditioned in situ for 2 h at the reaction temperature in a flowing stream of ultrapure nitrogen (Matheson). Ethanol (99.7%, BDH) was then continuously delivered from a reservoir by a calibrated piston pump, into a prevaporization zone from where it was blown over the catalyst bed by nitrogen flowing at 20 cm^3/min. The products were collected after 1 h on stream. Fixed temperature runs were performed at 385°C while fixed space velocity runs were done at 6.45 g-EtOH/g-feed h. Liquid products were collected using a condensation trap (which was cooled in ice) fitted to the outlet of the reactor tube and the gaseous products leaving the condensation trap were collected by the displacement of brine from a tower. Gaseous products were sampled using an evacuated Sulpelco gas sampling bulb (125 cm^3) and analysed using a Porapak Q stainless steel packed column (4 ft × 1/8 in) installed in the GC. Calibration was done using 99 mol% propane (Matheson). The liquid organic product was analysed on a 30M SE-30 capillary column (0.25 mm i.d. × 0.25 mm film thickness) installed in a Varian 3700 GC fitted with a flame ionization detector and a Varian 3400 GC coupled to a Finnigan ion trap 800 mass spectrometer.

3. Results and discussion

3.1. PROPENE FORMATION

Below 300°C, ethylene accounted for over 90% of the gaseous product (fig. 1). As the reaction temperature was increased the gradual increase in the concentration of C_3 (propene + propane) and drastic decrease in the concentration of C_2 (ethylene + ethane) and C_4 (butenes + butanes) products indicated that the process became more selective for C_3 species at higher temperatures. This suggests that C_3 species are not intermediate products between the formation of C_2 and C_4 species. The cracking of C_4 to give equimolar concentrations of C_3 and C_1 (methane) which would involve the formation of a very unstable primary carbenium ion is not deemed probable and the very low concentration of methane in the gaseous product justifies this. It is therefore likely that, as the reaction temperature was increased, C_4 was further polymerized to higher olefins, some of which were cracked into C_3 species while the others cyclized and aromatized. One posssible ole-

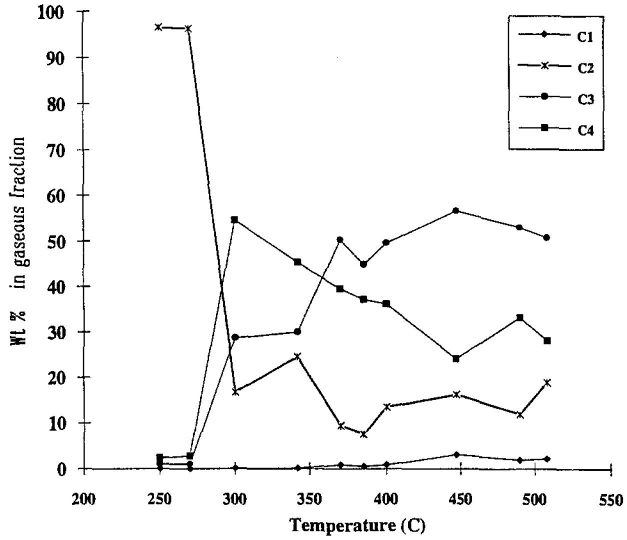

Fig. 1. Variation in wt% of species in gas fraction versus temperature.

fin involved in the cracking process is 4-methylpentene which was the most observed C_6 olefin in the liquid product. With ethanol conversion increasing from 88% at 250°C to 100% at temperatures above 300°C, evidence for this cracking can be observed in fig. 2. The figure shows that the concentration of liquid product, which was maximized at 300°C, decreased gradually as the temperature was increased over the range where cracking of C_6 species is favourable [15].

Further evidence in support of the formation of C_3 from cracking can be

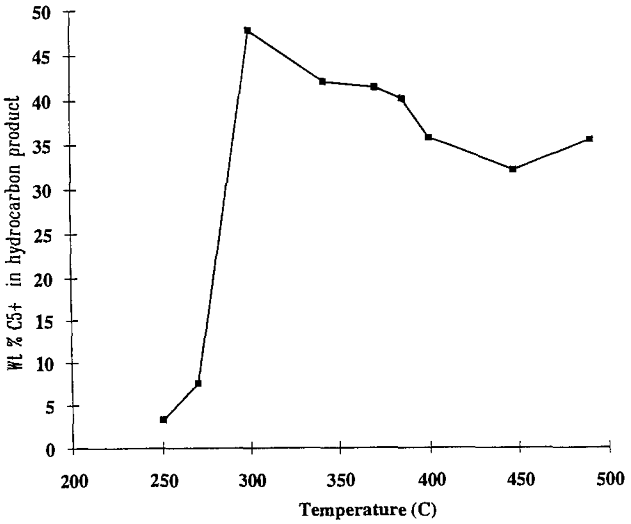

Fig. 2. Variation of wt% C_{5+} in hydrocarbon product versus temperature.

observed in fig. 3. With 100% ethanol conversion maintained, the figure shows that the amount of C_3 species in the gaseous product decreased progressively with extended time on stream to 1000 min. However, the concentration of both C_4 and C_2 species increased with time up to 300 min, after which C_4 decreased at a similar rate to C_3 while C_2 continued to accumulate significantly. These trends are attributed to the deactivation of the catalyst active sites from the deposition of polynuclear aromatics species (coking), as was confirmed by ^{13}C CP MAS/NMR. Consequently, the conversion of C_4 species to C_3 precursors was reduced with increasing time on stream, hence an initial accumulation of C_4 species. Similarly, the C_2 to C_4 conversion process was also affected hence a build up in C_2 species with time. After 300 min on stream, it could be that the rate of conversion of C_2 to C_4 was less than that of C_4 to C_6, hence a net accumulation of C_2 and a corresponding reduction in the concentration of C_4 species.

3.2. CORRELATION BETWEEN AROMATIZATION AND HYDROGENATION

The formation of naphthenes and aromatics during ethanol conversion results in the elimination of hydrogen which may be used up in the saturation of olefins through hydrogen transfer reactions or it may be released as dihydrogen. Fig. 4 shows that with an increase in the reaction temperature, the propane/propene ($C_3^-/C_3^=$) ratio increased gradually, indicating progressive saturation of $C_3^=$. By comparison, the levels of saturation of other olefins (ethylene and butenes), as shown by their relatively low paraffin/olefin ratios, were far less pronounced. The

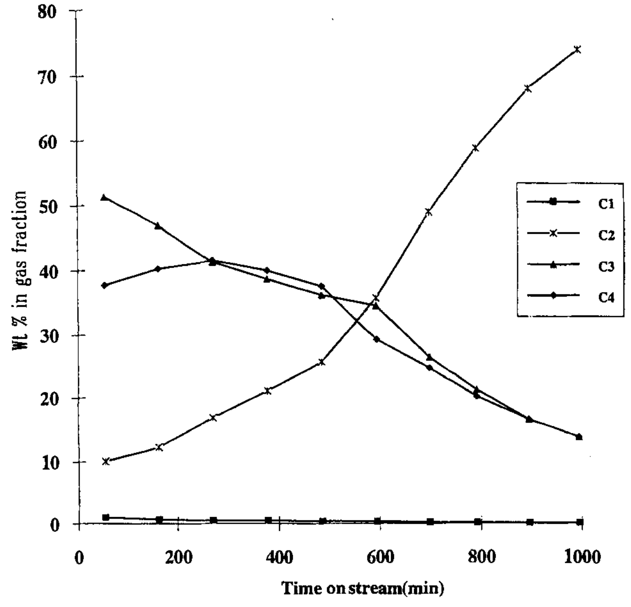

Fig. 3. Variation in wt% of species in gas fraction versus time on stream.

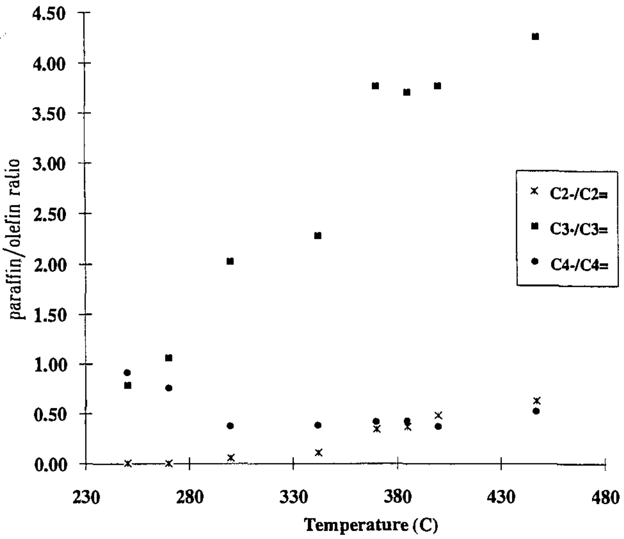

Fig. 4. Variation of paraffin/olefin ratios versus temperature.

preferred hydrogenation of propene over other olefins is a result of the parallel formation of this C_3 species along with aromatics during the conversion of the proposed C_6 moiety, which means that propene is always available in significant concentration during aromatization. Table 1 shows a comparison between the total paraffin/olefin ratio of the gaseous product and the percentage aromatics present among the hydrocarbons produced at increasing time on stream. The table shows that the overall paraffin/olefin ratio decreased as aromatization decreased and hence justifies the aromatization–hydrogen transfer process. Fig. 5 however, shows that propene was by far the main gaseous product participating in this process while ethylene and butene were much less affected. A similar conclusion can be

Table 1
Comparison between the $C^-/C^=$ ratio and total aromatics at various times on stream

Time on stream (min)	$C^-/C^=$ ratio	Percent aromatics in hydrocarbons
54	5.76	35.64
162	3.67	32.42
270	2.29	28.43
378	1.68	22.10
486	1.21	21.03
594	0.99	16.80
698	0.77	11.87
792	0.69	11.42
886	0.64	4.46
995	0.58	4.13

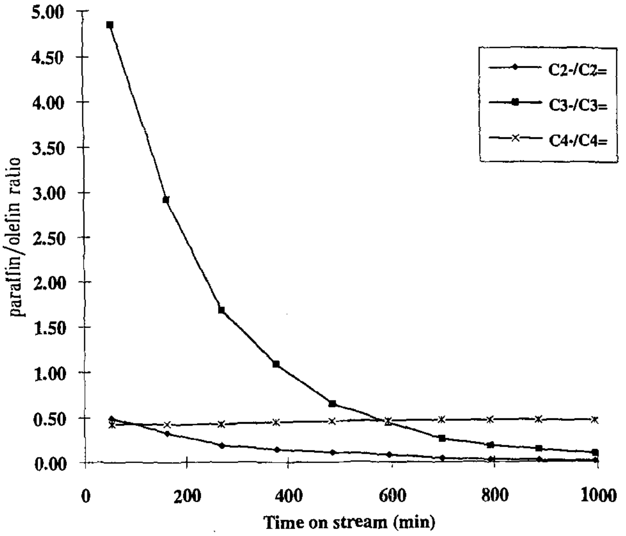

Fig. 5. Variation of paraffin/olefin ratios versus time on stream.

drawn from fig. 6, which shows that as the space velocity of the ethanol was increased, resulting in reactants spending less time on the active sites of the catalyst, again the propane/propene ratio was the only one significantly affected.

Finally, fig. 7 shows the change in the concentration of C_3 species versus time on stream. Though the total C_3 species decreased with increasing time on stream, propane decreased over the entire time period investigated while there was an accumulation of propene up to 600 min on stream, signifying a reduction in the hydroge-

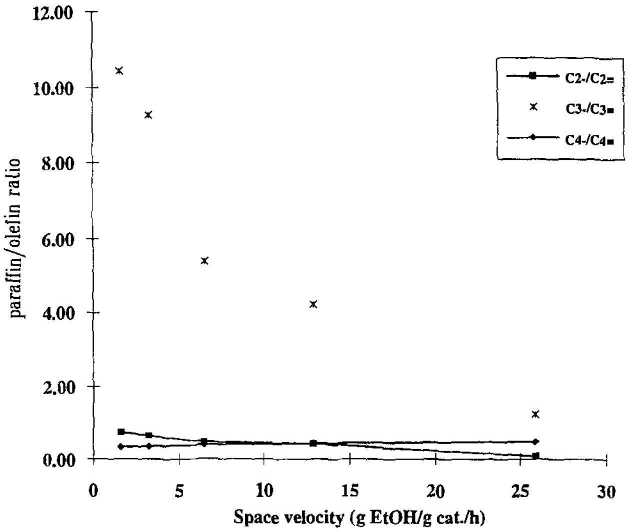

Fig. 6. Variation of paraffin/olefin ratios versus ethanol space velocity.

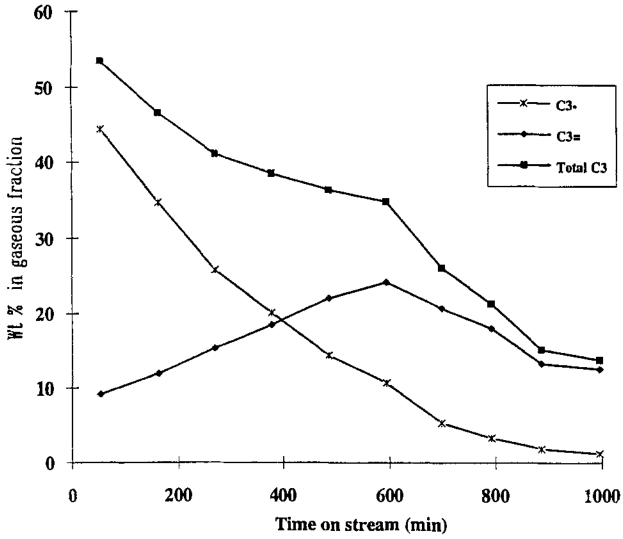

Fig. 7. Variation of wt% C_3 species in gas fraction versus time on stream.

nation process. Beyond 600 min the rates of decline of both the hydrogenation process and propene formation from cracking of C_6 moiety, became similar.

4. Summary

It can be summarized that during the conversion of ethanol to hydrocarbons on H-ZSM-5: (i) Propene is formed in significant amount from the cracking of C_6 moiety (possibly 4-methylpentene) and is not produced as an intermediate between C_2 and C_4 formation. (ii) As a result of the parallel formation of propene and aromatics, significant hydrogen transfer activity takes place between them resulting in the saturation of primarily propene while the other olefins played a less significant role.

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