# The Conversion of Ethene and Propene to Higher Hydrocarbons over ZSM-5

## INTRODUCTION

The acid-catalysed polymerisation of lower olefins is an important refinery operation aimed at obtaining gasoline range hydrocarbons from light, olefin rich gases (*1*). A product with a higher motor octane number can be obtained by olefin conversion over ZSM-5 zeolites which enable aromatic formation (*2*). Light olefins are also claimed to be intermediates in the conversion of methanol into gasoline (*3*). The fundamental chemistry of the reactions of olefins with ZSM-5 zeolite is thus worthy of study.

When olefins are passed over Brønsted acid catalysts, such as silica–alumina or zeolites, carbonium ion formation induces oligomerisation, isomerisation, cracking, and hydrogen transfer to give a broad range of products (*4, 5*). Despite the relatively simple model of consecutive reactions, the observation of primary products is remarkably illusory, and in many instances only the less strongly sorbed alkanes are observed as principal products (*6*).

A preponderance of propene oligomers in the product can be observed when operating at relatively low temperature (ca. 200°C), high space velocity and relatively high pressure (ca. 3.4 MPa) (*7*). Such work provides evidence for the oligomerisation step followed by the isomerisation and cracking of the oligomer to intermediate carbon number olefins.

Further evidence for the nature of primary products can be obtained by ir spectroscopic studies (*8*), thermogravimetric studies (*9*), and $^{13}C$ NMR (*10*).

In this study we report our observations of the products formed from the conversion of ethene and propene over ZSM-5 catalysts at low conversions and low (<300°C) temperatures. From these observations we deduce some of the fundamental processes of olefin oligomerisation, isomerisation, cracking, and hydrogen transfer.

## EXPERIMENTAL

Details of the preparation and characterisation of the zeolite samples have been previously described (*11*). Three samples were used in this study. One, a silicalite, contained only trace quantities of aluminium (≤0.01 wt%) and was obtained as large (20 $\mu$m) crystals. Another, ZSM-5(95), had a silica/alumina ratio of about 95 and comprised crystals of mixed size (between 1 and 10 $\mu$m). The third, ZSM-5(40), contained a high level of aluminium, silica/alumina = 40, and comprised aggregates of microcrystals (<0.1 $\mu$m crystals). The zeolites were transformed into the hydrogen form by a combination of washes with ammonium nitrate and calcination to 500°C. Before use the zeolites were compacted, in the absence of any binders, then crushed, and a 40- to 100-$\mu$m size range extracted.

Performance was monitored on a multichannel microreactor which has been described elsewhere (*12*). Catalyst (1 g) was charged into reactor tubes and the performance monitored for olefin conversion. The olefin was used without dilution, its purity being checked by a blank run. Product separation was obtained on a 50-m BP1 capillary column which enabled most individual products to $C_6$ to be identified by comparison with standards or with the aid of a mass spectrometer as a detector. Only 1-butene and isobutene co-eluted. In order

to determine the ratio of 1-butene to isobutene in the co-eluted peak, separate experiments were performed using a GC column with *n*-octane on Porasil C as packing which separated 1-butene from *trans*-2-butene and isobutene.

For the most part, olefin conversions were below 5%, when primary products would be expected to dominate.

The retention times of several hydrocarbons were determined in order to eliminate any problems in result interpretation due to the catalyst bed operating as a chromatographic column. A sample of ZSM-5(95) (1 g) was packed into a stainless-steel column (0.68 m × 32 mm). Hydrocarbons were then injected (1 μl of liquid or 100 μl of gas) onto the column held at 200°C and the eluting gases determined on a T.C.D. or F.I.D. When helium was used as a carrier gas the catalyst retained unsaturated molecules and chromatographically separated paraffins. To simulate reaction conditions, the column was equilibrated against a flow (40 ml min$^{-1}$) of propene (400 kPa) and nitrogen (400 kPa). The retention times of paraffins, olefins, and aromatics were very similar with no apparent likelihood of chromatographic separation. We thus conclude that when the catalyst is fully equilibrated against an excess of olefin, chromatographic effects on the catalyst do not occur to any appreciable extent.

Sorption of hexane and branched nonanes were determined on a C. I. Electronics Microbalance (1-g head) fitted with a conventional glass vacuum line as previously described (*11*).

### RESULTS

Aromatic formation was investigated by using the microreactor with a mass spectrometer as a gas-chromatographic detector and the ions with $m/z$ = 57, 55, and 91 monitored at various conversion temperatures. Only at temperatures over 300°C were significant quantities of $m/z$ = 91 observed, from which we deduce that aromatic formation was not significant below

ca. 300°C. Most results were obtained in the region 200–250°C which we judge to be well below that required for aromatic formation.

Propene conversion results for the three catalysts have been collated in Table 1. Early results (<15 min) were anomalous with conversion much higher than the rest of the run, the level of conversion increasing with alumina content. A drop-off in activity was observed for catalyst ZSM-5(95), which was left on stream for over 400 min at 204°C, indicating catalyst fouling. Silicalite and ZSM-5(95) produced $C_6$ olefin as the major olefinic component, but ZSM-5(40) produced predominantly $C_4$ and $C_5$ olefins. For silicalite $C_4$ and $C_5$ olefins were formed in approximately equimolar proportions suggesting a common $C_9$ intermediate. For ZSM-5(95) and ZSM-5(40), the $C_4$ olefin was slightly higher than the $C_5$ olefin, the excess $C_4$ probably arising from cracking of $C_{12}$ species. As the temperature was increased selectivity to linear $C_4$ and branched $C_5$ olefins was enhanced. The *trans*-$C_4$ olefin predominated over the cis isomer.

Ethene conversion results for ZSM-5(95) and ZSM-5(40) have been summarised in Table 2, with silicalite being inactive under similar conditions. Early results were also anomalous with the major products being the paraffins ethane, propane, and isobutane. Of the olefinic products the $C_4$ olefin was predominant. *Trans*-2-butene dominated over the cis isomer. $C_5$ olefins showed a high degree of branching. High values of $C_3$ olefin were formed on ZSM-5(40), this product increased with time-on-stream.

Both propene and ethene as feed produced significant quantities of paraffins presumeably as a result of H-transfer processes not directly associated with aromatics formation. Methane was very low or zero for both olefins.

For propene the dominant paraffin was isobutane, very little propane was formed. The percentage of isobutane in the product

TABLE 1

Selectivities (mole%); Propene Feed Gas (MHSV = 1 hr$^{-1}$)

| Catalyst | Silicalite | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Temperature (°C) | 204 | 204 | 204 | 204 | 204 | 214 | 225 | 236 | 247 | 256 |
| TOS (min) | 9 | 59 | 100 | 163 | 203 | 257 | 307 | 396 | 407 | 492 |
| % Conversion | 1.70 | 0.28 | 0.20 | 0.22 | 0.16 | 0.22 | 0.41 | 0.75 | 1.91 | 2.45 |
| $C_4$ olefin | 13.25 | 6.70 | 5.97 | 5.90 | 4.94 | 5.91 | 8.15 | 10.51 | 10.16 | 11.11 |
| $C_5$ olefin | 17.77 | 6.62 | 5.26 | 5.90 | 5.43 | 6.02 | 8.21 | 11.31 | 10.82 | 15.41 |
| $C_6$ olefin | 17.00 | 10.25 | 7.56 | 7.54 | 5.76 | 7.16 | 9.05 | 11.26 | 14.47 | 14.87 |
| Isobutane | 4.19 | 18.64 | 27.68 | 31.33 | 38.72 | 32.68 | 21.85 | 7.99 | 3.25 | 3.13 |
| *n*-butane | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Isopentane | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| *n*-pentane | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| *n*-hexane | 0.38 | 0.38 | 0.29 | 0.33 | 0.20 | 0.29 | 0.35 | 0.42 | 0.36 | 0.34 |
| $C_4$ Olefin selectivity (%) | | | | | | | | | | |
| Linear $C_4$ olefin | 77.56 | 32.84 | 22.07 | 28.33 | 27.51 | 20.09 | 41.12 | 52.28 | 68.61 | 70.69 |
| Branched $C_4$ olefin | 22.44 | 67.16 | 77.93 | 71.67 | 72.49 | 79.91 | 58.88 | 47.72 | 31.39 | 29.31 |
| $C_5$ Olefin selectivity (%) | | | | | | | | | | |
| Linear $C_5$ olefin | 86.54 | 90.48 | 100.00 | 93.33 | 90.91 | 92.86 | 91.18 | 86.59 | 82.74 | 83.42 |
| Branched $C_5$ olefin | 13.46 | 9.52 | 0.00 | 6.67 | 9.09 | 7.14 | 8.82 | 13.41 | 17.26 | 16.58 |
| Catalyst | ZSM-5(95) | | | | | | | | | |
| Temperature (°C) | 204 | 204 | 204 | 204 | 204 | 214 | 224 | 235 | 244 | 254 |
| TOS (min) | 10 | 64 | 112 | 164 | 423 | 957 | 1086 | 1192 | 1239 | 1281 |
| % Conversion | 28.45 | 2.62 | 1.87 | 1.71 | 0.53 | 1.04 | 3.47 | 3.01 | 5.60 | 11.95 |
| $C_4$ olefin | 8.79 | 10.64 | 10.16 | 9.40 | 9.16 | 10.09 | 13.62 | 15.03 | 15.43 | 15.93 |
| $C_5$ olefin | 7.83 | 9.62 | 9.18 | 8.59 | 7.50 | 8.28 | 11.01 | 11.78 | 12.78 | 13.24 |
| $C_6$ olefin | 7.14 | 13.51 | 13.43 | 14.05 | 16.05 | 14.80 | 11.81 | 12.30 | 11.49 | 9.76 |
| Isobutane | 6.51 | 5.29 | 7.10 | 8.58 | 15.64 | 12.18 | 2.70 | 2.68 | 1.67 | 1.11 |
| *n*-butane | 3.41 | 2.01 | 2.03 | 1.80 | 2.06 | 0.97 | 2.67 | 1.43 | 1.66 | 1.76 |
| Isopentane | 7.42 | 0.88 | 0.75 | 0.64 | 1.16 | 0.20 | 0.60 | 0.24 | 0.30 | 0.37 |
| *n*-pentane | 4.83 | 1.62 | 0.00 | 1.29 | 0.00 | 0.49 | 1.49 | 0.53 | 0.80 | 0.92 |
| *n*-hexane | 0.09 | 0.35 | 0.26 | 0.24 | 0.22 | 0.28 | 0.34 | 0.38 | 0.35 | 0.33 |
| $C_4$ Olefin selectivity (%) | | | | | | | | | | |
| Linear $C_4$ olefin | 69.04 | 66.88 | 64.50 | 64.05 | 61.35 | 60.59 | 73.07 | 73.08 | 74.36 | 74.62 |
| Branched $C_4$ olefin | 30.96 | 33.12 | 35.50 | 35.95 | 38.65 | 39.41 | 26.93 | 26.92 | 25.64 | 25.38 |
| $C_5$ Olefin selectivity (%) | | | | | | | | | | |
| Linear $C_5$ olefin | 59.39 | 76.44 | 76.34 | 76.92 | 84.09 | 80.49 | 77.92 | 77.84 | 74.37 | 68.31 |
| Branched $C_5$ olefin | 40.61 | 23.56 | 23.66 | 23.08 | 15.91 | 19.51 | 22.08 | 22.16 | 25.63 | 31.69 |
| Catalyst | ZSM-5(40) | | | | | | | | | |
| Temperature (°C) | 204 | 204 | 204 | 204 | 204 | 214 | 224 | 235 | 245 | 255 |
| TOS (min) | 14 | 51 | 111 | 147 | 187 | 315 | 375 | 435 | 495 | 555 |
| % Conversion | 51.30 | 3.56 | 1.61 | 1.74 | 1.68 | 2.93 | 5.53 | 10.49 | 19.08 | 47.74 |
| $C_4$ olefin | 11.08 | 12.41 | 9.52 | 13.91 | 17.05 | 18.05 | 16.15 | 14.85 | 15.97 | 17.01 |
| $C_5$ olefin | 8.40 | 11.31 | 13.68 | 13.12 | 11.46 | 12.15 | 13.11 | 12.53 | 13.47 | 13.93 |
| $C_6$ olefin | 5.42 | 9.16 | 13.69 | 13.49 | 12.35 | 12.14 | 11.81 | 9.84 | 9.71 | 6.31 |
| Isobutane | 1.10 | 1.59 | 3.13 | 3.50 | 3.37 | 2.20 | 1.52 | 1.06 | 0.90 | 0.75 |
| *n*-butane | 1.54 | 0.42 | 0.50 | 0.34 | 4.86 | 0.40 | 0.63 | 0.84 | 1.08 | 1.02 |
| Isopentane | 5.67 | 0.19 | 0.00 | 0.22 | 0.00 | 0.00 | 0.28 | 0.31 | 0.35 | 0.36 |
| *n*-pentane | 9.03 | 0.60 | 0.61 | 0.50 | 0.44 | 0.55 | 0.77 | 0.93 | 1.01 | 0.86 |
| *n*-hexane | 0.48 | 0.48 | 0.42 | 0.40 | 0.39 | 0.41 | 0.45 | 0.47 | 0.41 | 0.38 |
| $C_4$ Olefin selectivity (%) | | | | | | | | | | |
| Linear $C_4$ olefin | 77.50 | 70.95 | 100.00 | 65.84 | 46.78 | 50.72 | 64.49 | 70.13 | 73.66 | 75.52 |
| Branched $C_4$ olefin | 22.50 | 29.05 | 0.00 | 34.16 | 53.22 | 49.28 | 35.51 | 29.87 | 26.34 | 24.48 |
| $C_5$ Olefin selectivity (%) | | | | | | | | | | |
| Linear $C_5$ olefin | 67.87 | 82.89 | 83.33 | 83.55 | 83.41 | 82.83 | 81.66 | 79.21 | 75.97 | 71.41 |
| Branched $C_5$ olefin | 32.13 | 17.11 | 16.67 | 16.45 | 16.59 | 17.17 | 18.34 | 20.79 | 24.03 | 28.59 |

## TABLE 2

Selectivities (mole%); Ethene Feed Gas (MHSV = 1 hr$^{-1}$)

| Catalyst | ZSM-5(95) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Temperature (°C) | 204 | 204 | 204 | 204 | 204 | 204 | 214 | 214 | 226 | 235 |
| TOS (min) | 4 | 20 | 50 | 80 | 120 | 181 | 77 | 98 | 140 | 281 |
| % Conversion | 0.88 | 21.83 | 6.83 | 4.87 | 3.89 | 3.26 | 5.79 | 4.66 | 7.66 | 11.87 |
| $C_3$ olefin | 0.17 | 2.58 | 8.05 | 12.85 | 15.93 | 18.82 | 12.90 | 14.86 | 15.11 | 15.76 |
| $C_4$ olefin | 0.52 | 8.32 | 19.32 | 25.37 | 27.08 | 28.23 | 23.70 | 24.03 | 25.53 | 26.08 |
| $C_5$ olefin | 0.00 | 7.51 | 15.58 | 18.73 | 18.82 | 18.59 | 17.60 | 16.74 | 17.97 | 18.73 |
| $C_6$ olefin | 0.00 | 5.44 | 6.76 | 7.77 | 7.64 | 6.98 | 5.78 | 6.28 | 4.90 | 6.53 |
| Ethane | 91.46 | 9.99 | 15.45 | 0.00 | 0.00 | 0.00 | 13.76 | 16.54 | 12.49 | 6.68 |
| Propane | 3.30 | 1.87 | 0.61 | 0.56 | 0.52 | 0.52 | 0.65 | 0.61 | 0.68 | 0.71 |
| Isobutane | 3.57 | 11.39 | 1.48 | 1.20 | 0.99 | 0.82 | 1.25 | 1.03 | 1.16 | 1.11 |
| $n$-butane | 0.31 | 3.24 | 0.68 | 0.59 | 0.51 | 0.42 | 0.61 | 0.52 | 0.59 | 0.55 |
| Isopentane | 0.00 | 11.96 | 1.34 | 1.04 | 0.82 | 0.63 | 1.11 | 0.86 | 0.94 | 0.81 |
| $n$-pentane | 0.00 | 4.66 | 0.70 | 0.57 | 0.43 | 0.34 | 0.53 | 0.42 | 0.43 | 0.37 |
| $n$-hexane | 0.00 | 0.16 | 0.38 | 0.46 | 0.47 | 0.46 | 0.69 | 0.98 | 0.51 | 0.41 |
| $C_4$ Olefin selectivity (%) | | | | | | | | | | |
| Linear $C_4$ olefin | 100.00 | 49.56 | 53.42 | 55.37 | 56.30 | 56.91 | 55.47 | 55.98 | 55.90 | 56.25 |
| Branched $C_4$ olefin | 0.00 | 50.44 | 46.58 | 44.63 | 43.70 | 43.09 | 44.53 | 44.02 | 44.10 | 43.75 |
| $C_5$ Olefin selectivity (%) | | | | | | | | | | |
| Linear $C_5$ olefin | 0.00 | 14.05 | 16.15 | 17.19 | 17.72 | 18.17 | 17.88 | 17.72 | 18.78 | 19.86 |
| Branched $C_5$ olefin | 0.00 | 85.95 | 83.85 | 82.81 | 82.28 | 81.83 | 82.12 | 82.28 | 81.22 | 80.14 |
| Catalyst | ZSM-5(40) | | | | | | | | | |
| Temperature (°C) | 204 | 204 | 204 | 204 | 204 | 204 | 214 | 224 | 235 | 245 |
| TOS (min) | 5 | 66 | 222 | 261 | 349 | 406 | 466 | 526 | 586 | 646 |
| % Conversion | 1.21 | 5.58 | 3.17 | 3.10 | 2.75 | 2.94 | 5.09 | 8.87 | 16.61 | 28.97 |
| $C_3$ olefin | 1.46 | 11.55 | 19.93 | 20.77 | 23.12 | 22.15 | 23.00 | 22.53 | 18.46 | 14.76 |
| $C_4$ olefin | 0.00 | 25.16 | 22.80 | 22.64 | 23.55 | 22.40 | 25.83 | 28.77 | 26.92 | 25.84 |
| $C_5$ olefin | 0.00 | 19.14 | 13.81 | 13.42 | 13.38 | 12.16 | 15.05 | 17.62 | 17.76 | 18.53 |
| $C_6$ olefin | 0.00 | 8.57 | 5.43 | 5.24 | 5.14 | 4.62 | 5.79 | 6.71 | 6.89 | 7.44 |
| Ethane | 68.72 | 0.00 | 18.85 | 19.10 | 17.74 | 20.81 | 12.77 | 0.00 | 3.98 | 2.41 |
| Propane | 22.70 | 0.68 | 0.38 | 0.35 | 0.30 | 0.29 | 0.38 | 0.45 | 0.47 | 0.57 |
| Isobutane | 7.13 | 2.26 | 0.75 | 0.68 | 0.62 | 0.54 | 0.75 | 1.02 | 1.30 | 1.82 |
| $n$-butane | 0.00 | 0.94 | 0.32 | 0.30 | 0.26 | 0.22 | 0.31 | 0.37 | 0.40 | 0.53 |
| Isopentane | 0.00 | 1.95 | 0.61 | 0.55 | 0.48 | 0.41 | 0.56 | 0.74 | 0.92 | 1.28 |
| $n$-pentane | 0.00 | 1.06 | 0.33 | 0.29 | 0.24 | 0.20 | 0.25 | 0.31 | 0.32 | 0.41 |
| $n$-hexane | 0.00 | 0.55 | 0.41 | 0.40 | 0.38 | 0.34 | 0.44 | 0.52 | 0.54 | 0.58 |
| $C_4$ Olefin selectivity (%) | | | | | | | | | | |
| Linear $C_4$ olefin | 0.00 | 54.37 | 59.13 | 59.26 | 59.28 | 58.20 | 58.53 | 57.57 | 56.21 | 54.75 |
| Branched $C_4$ olefin | 0.00 | 45.63 | 40.87 | 40.74 | 40.72 | 41.80 | 41.47 | 42.43 | 43.79 | 45.25 |
| $C_5$ Olefin selectivity (%) | | | | | | | | | | |
| Linear $C_5$ olefin | 0.00 | 18.24 | 21.70 | 22.16 | 22.52 | 22.37 | 22.13 | 21.91 | 21.58 | 21.00 |
| Branched $C_5$ olefin | 0.00 | 81.76 | 78.30 | 77.84 | 77.48 | 77.63 | 77.87 | 78.09 | 78.42 | 79.00 |

decreased with increasing alumina content, i.e., ZSM-5(40) < ZSM-5(95) < silicalite; in weight terms all catalysts produced about the same quantities of isobutane. The isobutane content increased to a limit with time on stream, and fell with temperature and contact time.

For ethene the dominant paraffin was ethane, but significant quantities of propane were formed at early times-on-stream. Paraffin formation fell with time-on-stream. The dominant $C_4$ paraffin was isobutane.

## DISCUSSION

Our results indicate that in olefin conversion, ZSM-5 shows pronounced chromatographic properties which can perturb the

products observed until equilibrium with a reactant gas is achieved. After reasonable times on line, e.g., >15 min, three product types are observed, olefins, paraffins, and aromatics. Our results indicate that aromatic formation occurs at temperatures above 250°C and is significant at temperatures over 300°C. Some paraffins are formed at much lower temperatures, e.g., 200°C, and we deduce these arise from H-transfer processes not directly associated with aromatic formation. The principal products at low temperatures and reasonable times-on-stream are olefin oligomers and their cracked products.

For ethene and propene the major product is the dimer (either $C_4$ or $C_6$ olefin, respectively) but for catalysts with the highest alumina content (ZSM-5(40)) there are significant amounts of nondimer ($C_3$, $C_4$, and $C_5$ olefins, respectively). This increased cracking of higher olefins with increasing alumina content of the catalyst is consistent with their increasing activity.

On silicalite and ZSM-5 of relatively low alumina content, the $C_4$ and $C_5$ olefins derived from propene are formed in approximately equimolar proportions; this suggests they are derived from a common $C_9$ intermediate. As the temperature is increased there is a change in $C_4$ plus $C_5$ olefin selectivity with linear $C_4$ and branched $C_5$ olefins increasing. This is shown in Fig. 1 in which selectivities to the appropriate $C_4$ and selectivities to the appropriate $C_5$ olefins have been summed and changes with temperature shown. This leads to the view that a simple structural change occurs in the $C_9$ intermediate. We propose that at low temperatures, the $C_9$ precursor is based on a 2,4-dimethylheptane skeleton (I), which upon cracking at the 3–4 bond gives a branched $C_4$ and a linear $C_5$ product. At higher temperatures, isomerisation occurs to a $C_9$ precursor based upon a 2,5-dimethylheptane skeleton (II). Upon cracking at the 4–5 bond, a linear $C_4$ and a branched $C_5$ results.

## Propene over Silicalite

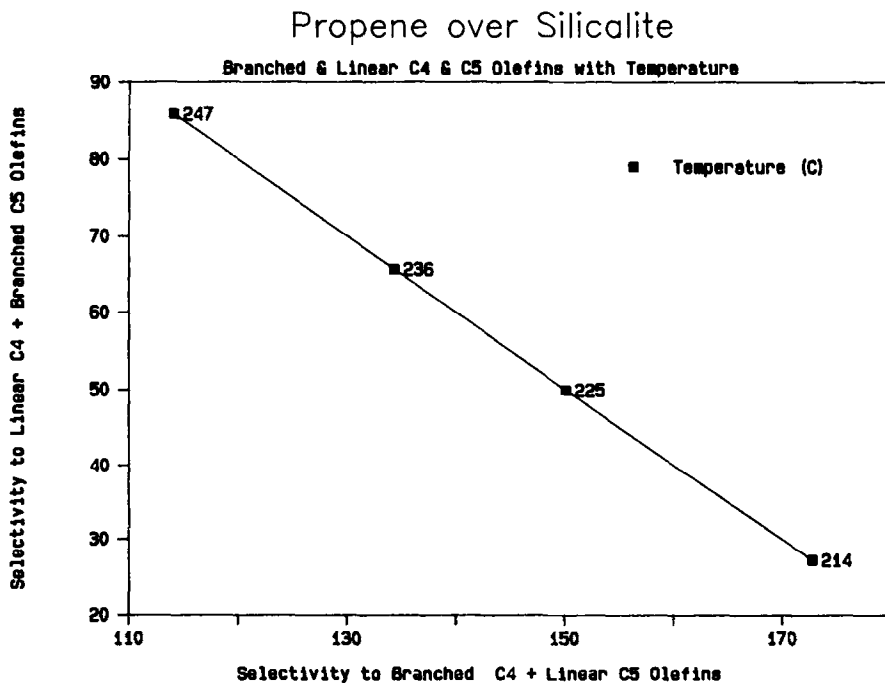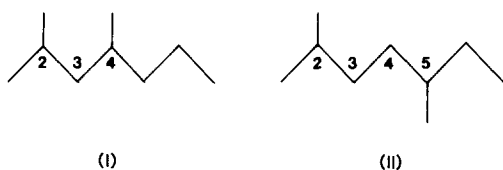### Branched & Linear C4 & C5 Olefins with Temperature



FIG. 1. Plot of selectivity to linear $C_4$ plus selectivity to branched $C_5$ olefins versus selectivity to branched $C_4$ plus selectivity to linear $C_5$ olefins for silicalite with increasing reaction temperature.

(I)                    (II)

Sorption experiments show that both the 2,4- and 2,5-dimethyl heptanes are accessible to the zeolite channel, the 2,4-isomer being slightly less so than the 2,5-isomer, hence showing both structures can be formed within the confines of the zeolite crystal.

The formation of isobutane from propene appears unrelated to olefin oligomerisation and cracking. The rise in isobutane level to a limiting value suggests that its formation is dependent upon the coformation of a coke precursor which is limited in extent by the confines of the catalyst. Isobutane formation would then occur by transfer of separate $CH_3$ and H species, from the coke precursor to the reacting olefin, rather than H-transfer to a $C_4$ product. The lack of sensitivity of isobutane formation to alumina content of the zeolite indicates a mechanism independent of Brønsted acidity and crystallite size.

This is not the case for ethene, since ethane is the principal alkane, although some propane is formed at early time-on-stream. Here the influence of the requirement for the olefin to form a primary carbonium ion may be felt, and the ethyl cation being readily able to abstract $H^-$ from a suitable substrate.

## CONCLUSIONS

For both ethene and propene conversion over ZSM-5, higher olefins intermediate in carbon number between monomer and oligomer are produced via cracking of higher oligomers. Isomerisation of intermediate carbonium ions can lead to different isomers but steric constraints placed bounds on the isomers observed. Formation of alkanes can be independent of hydrogen transfer processes which ultimately form aromatics. Hydrogen transfer can occur at

low temperature with low activation energy. The formation of isobutane in propene conversion may be best regarded as methyl and hydride group transfer from a coke precursor to monomer, rather than hydrogen transfer to a $C_4$ olefin.

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