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RESEARCH NOTE

Influence of Temperature on the Product Selectivity and Distribution of Aromatics and C_8 Aromatic Isomers in the Conversion of Dilute Ethene over H-Galloaluminosilicate (ZSM-5 type) Zeolite

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Product selectivity and distribution of the total and C_8 aromatics at the different isoconversions (40, 60, and 80%) of dilute ethene (5 mol% C_2H_4 in N_2) over the H-GaAlMFI zeolite catalyst at different temperatures (300–500°C) have been investigated. A strong temperature dependence of the selectivity for aromatics, propene, and C_4 hydrocarbons and also of the distribution of aromatics and C_8-aromatic isomers has been observed. At lower temperatures (below 400°C) the aromatization involved mainly hydride transfer reactions, but at higher temperatures (≥400°C) it involved mainly dehydrogenation reactions. The distribution of xylene isomers is controlled by steric factors at 300°C but kinetically at 500°C. © 2002 Elsevier Science

Key Words: **aromatization; ethene; H-galloaluminosilicate (ZSM-5 type) zeolite; product distribution.**

INTRODUCTION

Oxidative coupling of methane (OCM) to ethane and ethene is a process of great practical importance for the effective utilization of natural gas/methane. This process has been widely investigated in the past 15 years (1–4). One of the serious limitations of the OCM process is the low concentration of ethene in the product stream. Separation of ethene at a low concentration is not at all economical. This limitation of the OCM process can, however, be overcome by converting the ethene at a low concentration, without its separation, directly into much less volatile products like aromatic hydrocarbons, as disclosed by Choudhary *et al.* in two U.S. patents (5, 6) and also reported later by Qiu *et al.* (7).

A few studies have been reported earlier on the aromatization over H-ZSM-5 (8–10), and Zn-, Fe-, and Ga-modified ZSM-5 (11–15) zeolite catalysts. Zn- or Ga-modified ZSM-5 catalyst showed much better performance than the parent (H-ZSM-5) zeolite (12, 16). An earlier study (15) showed that Ga-impregnated H-ZSM-5 is an effective catalyst for the aromatization of dilute ethene at 500–550°C. In our very recent study (16), we have compared the different Ga-modified ZSM-5- type zeolite catalysts for the aromatization of dilute ethene and found that the most effective catalyst for this process is a H-galloaluminosilicate (MFI) zeolite. The high ethene aromatization activity of this zeolite catalyst is attributed to the uniformly distributed Ga–oxide species (which are formed *in situ* due to degalliation of the framework gallium of the zeolite) in the zeolite channels and also to the high acidity of the zeolite.

The present work was undertaken with the objective of thoroughly investigating the influence of temperature (at different space velocities) on the product selectivity/distribution in the aromatization of dilute ethene (5 mol% ethene in N_2) over H-galloaluminosilicate (MFI) zeolite having high concentrations of both zeolitic acidity and nonframework Ga–oxide species.

EXPERIMENTAL

The H-galloaluminosilicate (ZSM-5-type) or H-GaAlMFI zeolite used in the present work had the following chemical composition and properties:

Bulk composition	Si/Al = 37.5 and Si/Ga = 24.3
Framework composition	Si/Al = 40.3 and Si/Ga = 49.9
Crystal size	5.5 ± 1.5 μm
Crystal morphology	Near spherical
Nonframework Ga	0.32 mmol g^{-1}
Acid sites	0.46 mmol g^{-1} h^{-1} (measured in terms of pyridine chemisorbed at 400°C)

The preparation and characterization (by XRD, SEM, ^{71}Ga, ^{29}Si, and ^{27}Al MAS NMR, and chemical analysis) of the zeolite have been given elsewhere (16, 17). The

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concentration of nonframework Ga was obtained from the framework and bulk concentrations of Ga in the zeolite (16). The framework Ga concentration was obtained from the framework Si/(Ga + Al) (determined from ^{29}Si MAS NMR) and Si/Al (determined from the bulk Al and octahedral Al obtained from ^{27}Al MAS NMR) ratios. The 52- to 72-mesh-size particles of the zeolite were pretreated in a flow of hydrogen (1030 $cm^3 g^{-1} h^{-1}$) at 600°C for a period of 1 h and then in a flow of air for 0.5 h.

Aromatization of ethene over the zeolite catalyst was carried out at atmospheric pressure in a continuous flow quartz reactor (13-mm i.d.) provided with a chromel–alumel thermocouple in the center of the catalyst bed (containing 0.2 g zeolite catalyst diluted uniformly by an inert solid, the total volume being 1 ml), using 5 mol% ethene in N_2 as a feed. The conversion and selectivity data at different temperatures (300–500°C) and space velocities (3100–49,500 $cm^3 g^{-1} h^{-1}$, measured at 0°C and 1 atm pressure) were obtained by a square pulse technique by passing the reaction mixture over a fresh catalyst bed for a short period (2–5 min) under steady-state conditions and then replacing the reactant mixture by a stream of pure N_2 during the period of product analysis. At the end of the square pulse experiment, the reaction products were sampled using a heated gas sampling valve and analyzed by a GC with FID, using Porapak-Q (3 mm × 3 m), Benton-34 (5%), and dinonylphthalate (5%) on Chromosorb-W (3 mm × 5 m) columns. The absence of catalyst deactivation in the step pulse experiments was confirmed by repeating the first experiment. The C and H balance in all the experiments was 95% and above.

RESULTS AND DISCUSSION

Representative results showing a strong influence of ethene conversion on the product selectivity and the distribution of aromatics and C_8 isomers in the aromatization of dilute ethene over the zeolite catalyst at 350°C are presented in Fig. 1.

Because of the observed strong influence of conversion (Fig. 1), it is essential to compare the product selectivity/distribution at the same conversion (i.e., isoconversion) for knowing the true effect of the reaction temperature on the product selectivity/distribution. Hence, the ethene aromatization data for each temperature were collected at different space velocities, and from these results the data on the product selectivity/distribution at three different isoconversion levels (40, 60, and 80%) were obtained. Results showing the influence of temperature on the product selectivity, the H_2 produced per mole of ethene converted to aromatics, the distribution of aromatics and C_8 isomers, and the *p*-xylene/*m*-xylene and *p*-xylene/*o*-xylene ratios at different isoconversion levels are presented in Figs. 2–5.

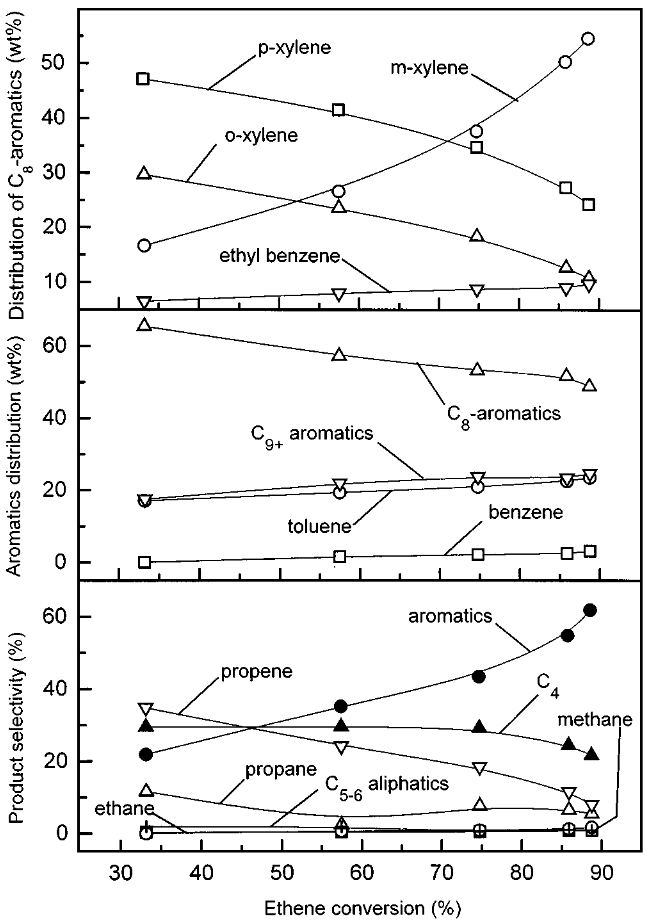

FIG. 1. Dependence of product selectivity and distribution of aromatics and C_8-aromatic isomers on the conversion in the ethene aromatization (at 350°C).

Effect of Temperature on Product Selectivity

From the results in Fig. 2, the following important observations on the temperature dependence of the product selectivity at the three different isoconversion levels can be made. When the temperature is increased, (i) The aromatics selectivity is very markedly increased; (ii) the selectivities for C_4, $C_{5–6}$, and propene are decreased; and the decrease of the C_4 hydrocarbon selectivity is very appreciable; (iii) the selectivities for ethane and methane are increased, but the increase is small; (iv) the propane selectivity at the high conversion levels is affected, but only to a small extent.

The previous observations show a strong influence of temperature on the selectivity of aromatics. The formation of aromatics is more and more favored at higher temperatures.

It is interesting to note from the results in Fig. 3 that the H_2 formed in the ethene-to-aromatics conversion is increased very markedly by increasing the temperature. The observed very small amount of H_2 formed at 300°C indicates that the ethene aromatization at this temperature involves mainly hydrogen transfer reactions (catalyzed by the

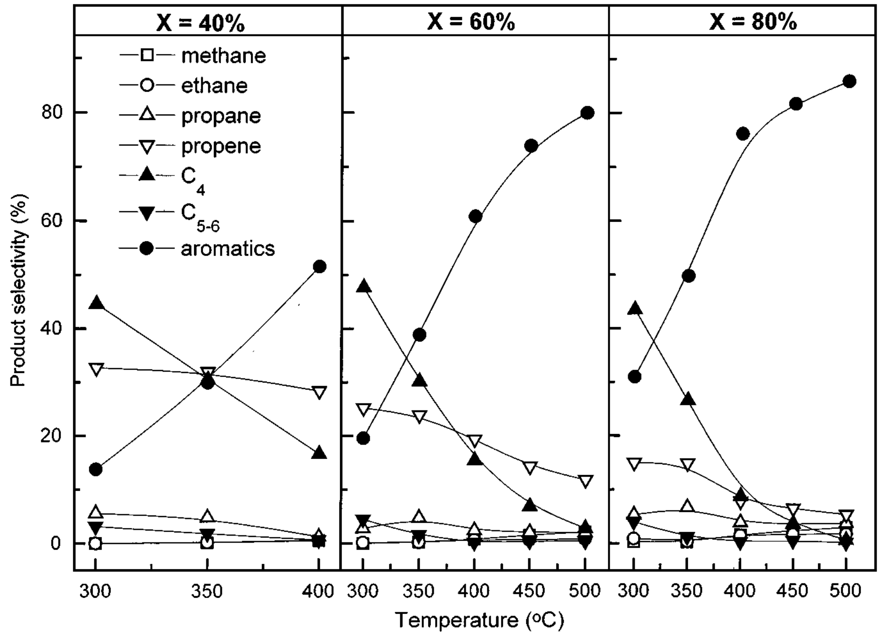

FIG. 2. Effect of temperature on the product selectivity in the ethene aromatization at three different isoconversions.

zeolitic acid sites) leading to the formation of alkanes from olefins, with almost no dehydrogenation reactions. On the contrary, at ≥400°C the H_2 produced in the aromatization is quite large, indicating the occurrence of dehydrogenation reactions catalyzed by the nonframework Ga–oxide species in combination with the zeolitic acid sites. At the intermediate temperature (350°C), both hydrogen transfer and dehydrogenation reactions seem to play important roles in the aromatization.

The high aromatics selectivity at higher temperatures (≥400°C) is attributed to the high dehydrogenation activity of the catalyst at higher temperatures. At lower temperatures (300°C), the catalyst showed little or no dehydrogenation activity. The formation of aromatics is thus

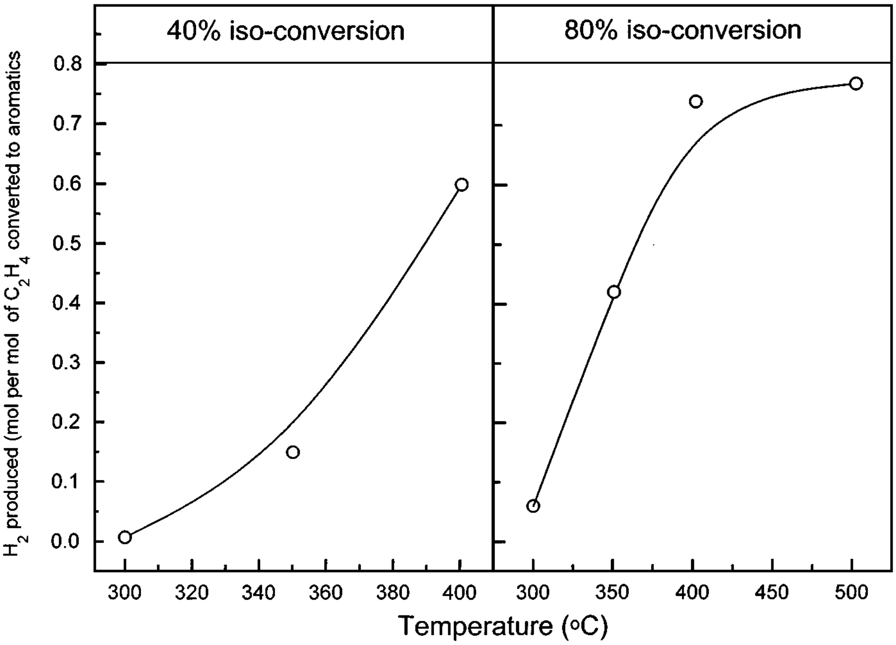

FIG. 3. Effect of temperature on the H_2 produced per mole of C_2H_4 converted to aromatics in the ethene aromatization at two different isoconversions.

controlled by hydride transfer reactions at lower temperatures (300°C), by dehydrogenation reactions at higher temperatures (≥400°C), and by both reactions at intermediate temperatures.

The formation of propene to an appreciable extent is expected mostly by the symmetrical scission of the C_6 oligomer and that of propane by the hydride transfer reaction of propene with ethene oligomers/naphthenes. C_4 hydrocarbons are formed with high selectivity at lower temperatures, mostly by the dimerization of ethene and hydride transfer reactions of the ethene dimers (butenes) with oligomers/naphthenes. With increasing temperatures, the selectivity for propane and C_4 hydrocarbons is decreased due to a decrease in the hydride transfer reactions and also because of their transformation into aromatics at higher temperatures. The formation of C_{5-6} hydrocarbons is quite small and moreover observed only at lower temperatures (<400°C). This is expected because of the high reactivity of C_{5-6} hydrocarbons over the catalyst at higher temperatures. The formation of methane is very small and observed only at higher temperatures mostly due to dealkylation of aromatics and cracking of ethene oligomers. The observed decrease in the selectivity for propene and C_4 and C_{5-6} hydrocarbons with increasing temperatures is consistent with the fact that the aromatization of these hydrocarbons is favored at higher temperatures.

Effect of Temperature on Aromatics Distribution

The results in Fig. 4 show a strong influence of the temperature on the aromatics distribution at the three different isoconversion levels.

When the temperature is increased, the concentration of different aromatics in the total aromatics formed in the ethene aromatization is changed as follows. (i) The formation of C_8 aromatics is decreased; the decrease is very sharp at the higher temperatures (>400°C). (ii) The concentration of C_{9+} aromatics is also decreased; the decrease is, however, pronounced at the lower temperatures. (iii) The concentration of toluene is increased markedly. (iv) The concentration of benzene is increased exponentially.

The order of the formation of different aromatics at the lowest and highest temperatures are as follows: At 300°C

$$C_8 \text{ aromatics} \gg C_{9+} \text{ aromatics} > \text{toluene} \gg \text{benzene}.$$

At 500°C

$$\text{toluene} > \text{benzene} > C_8 \text{ aromatics} \geq C_{9+} \text{ aromatics}.$$

The previous orders of the formation of different aromatics at low and high temperatures indicate that the aromatics distribution is not controlled or at least not strongly influenced by the diffusion of reaction species in the zeolite channels, although the zeolite crystals are quite large ($5.5 \pm 1.5 \mu m$). In the case of diffusion control, at the lowest temperatures (300°C), the formation of fast diffusing species (i.e., benzene and toluene) would have been favored over that of the slow diffusing species (i.e., C_8 and C_{9+} aromatics). The observed increased formation of benzene and toluene at higher and higher temperatures is expected mostly because of the increased dealkylation of C_8 and C_{9+} aromatics with increasing temperatures. The results thus indicate that the aromatics distribution, particularly at higher

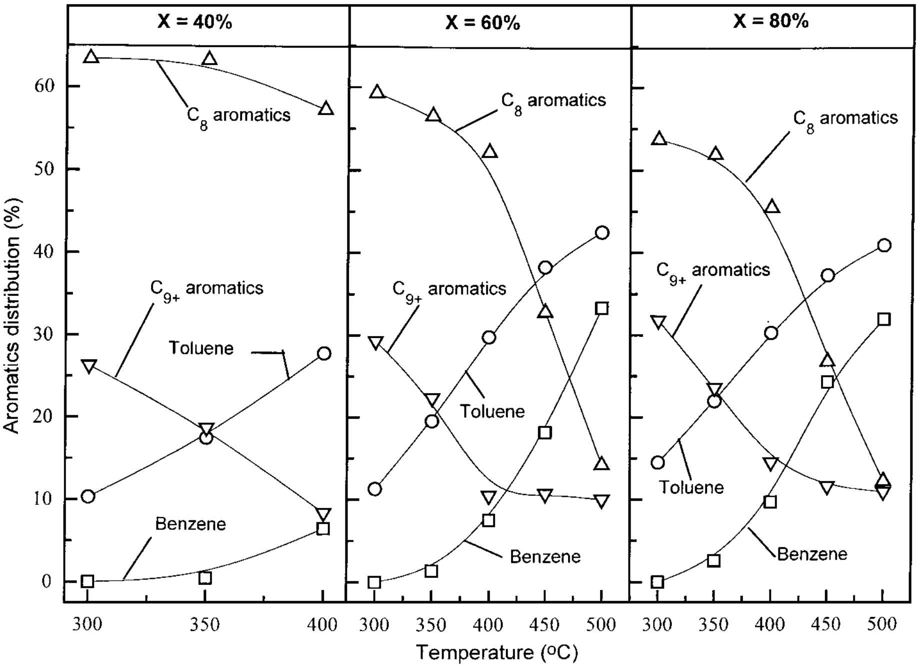

FIG. 4. Effect of temperature on the distribution of aromatics in the ethene aromatization at three different isoconversions.

temperatures, is controlled mostly by the aromatics transformation reactions, particularly by the demethylation of the methyl benzenes with the formation of methane (in the presence of H_2). The observed increase in the selectivity for methane formation with increasing temperatures (Fig. 2) is consistent with this. The demethylation of methyl benzenes may also involve the formation of ethene by the coupling of methylene radicals under hydrogen-deficient conditions, particularly at lower temperatures. The demethylation reactions are thermodynamically favored at all reaction temperatures (300–500°C).

Effect of Temperature on the Distribution of C_8 Aromatics

The relative concentration of *p*-xylene, *o*-xylene, *m*-xylene, and ethylbenzene is strongly influenced by the reaction temperature (Fig. 5). By increasing the temperatures, the concentrations of *p*-, *o*-, *m*-xylenes, and ethylbenzene in the C_8 aromatics are influenced as follows: (i) The concentration of *p*-xylene is decreased appreciably. (ii) The concentration of *o*-xylene is also decreased, but the decrease is very sharp. (iii) The concentration of *m*-xylene is increased very markedly. (iv) The concentration of ethylbenzene is also increased up to the temperature of 400°C and then leveled off. Also, at all the isoconversions, the *p*-xylene/*m*-xylene ratio is decreased, but the *p*-xylene/*o*-xylene ratio is increased very sharply with increasing temperatures (e.g., at 40% isoconversion, at 300, 350, and 400°C, the *p*-xylene/*m*-xylene = 7.5, 2.3, and 1.6, respectively, and *p*-xylene/*o*-xylene = 1.1, 1.6, and 4.2, respectively).

The temperature dependence of the distribution of C_8 aromatics is quite complex. At 300°C, the concentration of all four C_8 aromatics (except ethylbenzene for the isoconversion of 80%) is far from that expected at the thermodynamic equilibrium. The equilibrium concentration of ethylbenzene, *p*-xylene, *m*-xylene, and *o*-xylene is 5, 23, 51, and 21%, respectively, at 300°C; and 10, 21, 46, and 23%, respectively, at 500°C (18).

The increase of the ethylbenzene concentration with the ethene conversion (Fig. 1) and temperature (Fig. 5) indicates that ethylbenzene is not formed as a primary aromatic hydrocarbon from a C_8 oligomer; it is formed most probably by the ethenation of benzene.

At 300°C, the order for the formation of xylene isomers is as follows: *p*-xylene > *o*-xylene > *m*-xylene. This order is the same as that for the diffusivity of the xylene isomers in H-ZSM-5 (19). Because of the presence of non-FW Ga oxide species in the zeolitic channel, as compared to H-ZSM-5, the H-GaAlMFI zeolite is expected to show a stronger effect on the relative diffusivity of xylene isomers. The observed trend for the formation of xylene isomers indicates a strong influence of steric hindrance for the formation of xylene isomers, particularly on the formation of *m*-xylene, in the zeolite channels at 300°C. However, the influence of steric hindrance is reduced by increasing the temperatures, allowing the isomerization of *p*- and *o*-xylenes to *m*-xylene. It is, however, very interesting to note that the concentration of *m*-xylene is increased from 27.7 to 65.6% (which is above the thermodynamic equilibrium value, 46%), and that of *o*-xylene is decreased from 30.6 to 1.2% (which is much

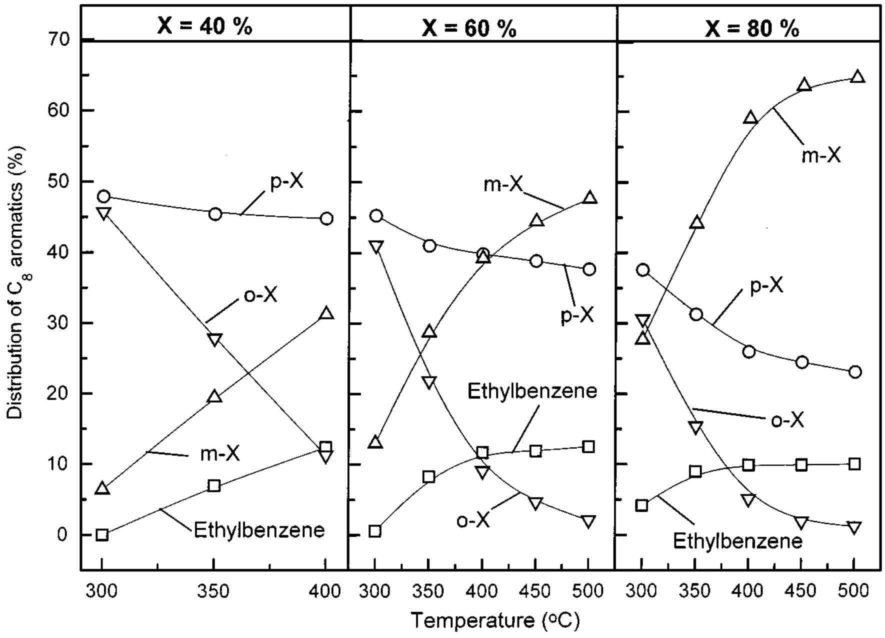

FIG. 5. Effect of temperature on the distribution of C_8-aromatic isomers in the ethene aromatization at three different isoconversions.

below the thermodynamic value, 23%), by increasing the temperature from 300 to 500°C (Fig. 5, third panel on the right). This shows that the formation of *m*-xylene is caused mostly by the isomerization of *p*- and *o*-xylenes, and it is controlled kinetically, particularly at higher temperatures.

CONCLUSIONS

From the present studies on the temperature dependence of product selectivity and distribution of aromatics and C_8 aromatic isomers at different isoconversion levels in the aromatization of dilute ethene over H-GaAlMFI zeolite, the following important conclusions have been drawn.

1. The product selectivity, particularly the selectivity for aromatics, propene, and C_4 hydrocarbons, and the distribution of aromatics are strongly influenced by the temperature.
2. In the aromatization, hydride transfer reactions are predominant at lower temperatures (below 400°C). But at higher temperatures the dehydrogenation reaction becomes predominant, producing an appreciable amount of H_2.
3. The distribution of C_8 aromatic hydrocarbons is also very strongly influenced by the temperature. It is controlled mostly by the steric factors at lower temperatures, but it is controlled kinetically at higher temperatures (500°C).

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