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Influence of space velocity on product selectivity and distribution of aromatics in propane aromatization over H-GaAlMFI zeolite

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Abstract

Aromatization of propane has been investigated over H-GaAlMFI zeolite at different space velocities (1500–49,000 $cm^3/g/h$) in the temperature range of 450–600 °C. The product selectivity and aromatic distribution was profoundly influenced by the space velocity. The aromatization/cracking ratio was found to pass through a maximum in the space velocity range of 5000–12,000 $cm^3/g/h$ at all the investigated temperatures. Selectivity for toluene increased, while that for benzene decreased with increasing aromatic yields (decreasing space velocity). Selectivity for C_8 and C_9 aromatic compounds passed through a maximum with increasing aromatic yields. The *p*-xylene selectivity decreased with increasing aromatic yields, while that for *m*-xylene increased. The following reaction pathway for the propane aromatization reaction over H-GaAlMFI has been proposed based on the observed product distribution. Propylene is the primary (intermediate) product of the propane aromatization reaction. Ethene is formed by the primary cracking of propane as well as from cracking of higher olefins. Benzene, *p*-xylene, and ethyl benzene are primary aromatic products, while *m*-xylene, *o*-xylene and C_9 compounds are formed via secondary transformations. Toluene is formed as a primary aromatic product and from secondary transformations.

Keywords: Propane aromatisation; Space velocity; Ga-based zeolites; ZSM-5; Selectivity; Aromatics

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1. Introduction

Aromatization of lower alkanes (C_2, C_3 and C_4), which is a process of significant commercial importance, has been investigated over a variety of Ga-based ZSM-5 type zeolites, viz. physically mixed Ga_2O_3 and H-ZSM-5, Ga-exchanged or Ga-impregnated H-ZSM-5 (Ga/H-ZSM-5) [1–3], H-Gallosilicates (GaMFI) [4–10], and H-Galloaluminosilicate (H-GaAlMFI) [11]. Amongst the various Ga-modified zeolites (Ga/HZSM-5, H-GaAlMFI and GaMFI), GaAlMFI shows the highest activity/selectivity for the propane aromatization process [11]. The superior performance of these zeolites has been attributed to the presence of highly dispersed Ga species in combination with strong zeolitic acid sites [12]. Our previous studies have shown that the product selectivity and the aromatic distribution in propane aromatization over H-GaMFI are very strongly influenced by the space velocity [13]. However, the effect of space velocity on the more active H-GaAlMFI zeolite for the propane aromatization reaction has not yet been reported. In this work, the effect of space velocity on product selectivity and distribution of aromatics in propane aromatization over H-GaAlMFI zeolite has been investigated at different temperatures. A mechanism for the propane aromatization reaction over H-GaAlMFI zeolite has been put forth, based on the results observed in this study.

2. Experimental

2.1. Catalyst synthesis

H-GaAlMFI zeolite was synthesized by the hydrothermal crystallization from a gel consisting of Na-trisilicate (Fluka), gallium nitrate (Aldrich), aluminium nitrate (BDH), TPA-Br (Aldrich), sulfuric acid and deionized water in a stainless steel autoclave at 180 °C for 96 h [12]. The zeolite crystals were washed thoroughly with deionized water and dried at 120 °C for

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10 h. After calcination at 550 °C for 15 h under static air, it was converted into its NH_4 form by repeated exchanging with 1 M ammonim nitrate solution at 80 °C. H-GaAlMFI was obtained by deammoniation of its NH_4 form by calcination at 600 °C (or 700 °C) for 1 h in a flow of moisture free nitrogen (1800 cc/g/h). The catalyst was treated in H_2 flow for 1 h followed by calcinations in moisture free air for 30 min. Unless mentioned otherwise the zeolite sample obtained by deammoniation by calcination at 600 °C has been used for this propane aromatization study.

2.2. *Catalyst characterization*

The framework (FW) composition of the zeolite was determined by NMR instrument (using a Bruker MSL300 MHz NMR, 2 μs pulse, flip angle of 45°, and samples spun at 3–3.5 kHz). The FW Si/(Ga + Al) ratios were determined from ^{29}Si MAS NMR and the individual FW Si/Al and Si/Ga ratios were estimated from the FW Si/(Ga + Al), octahedral Al (determined from ^{27}Al MAS NMR) and bulk concentration of Al in the zeolite [14]. The strong acidity of the zeolite samples was measured in terms of pyridine chemisorbed at 400 °C. The chemisorption of pyridine has been defined as the amount of pyridine retained by a presaturated zeolite after it has been swept with pure nitrogen for a period of 4 h. Details of the procedure to determine acidity by this method have been described earlier [8]. The MFI structure of GaAlMFI was confirmed by XRD and FTIR analysis [15].

2.3. *Activity tests*

The propane aromatization reaction was carried out in an atmospheric pressure continuous flow quartz reactor equipped with a Chromel–Alumel thermocouple in the center of the catalyst bed (1 g catalyst and 1:1 propane–N_2 mix as feed). The conversion and selectivity data at different space velocities (1500–49,000 cc/g/h) and temperatures (450–600 °C) were obtained in the absence of catalyst deactivation (initial activity and selectivity). This was accomplished by employing the square pulse technique by passing the reaction mixture over a fresh catalyst for a short period (2–5 min) under steady state and then replacing the reaction mixture with pure N_2 during the period of product analysis. The reaction products were analyzed by an on-line GC with FID, using Poropak-Q (3 mm × 3 m) and Benton-34 (5%) and dinonylthalate(5%) on Chromosorb-W (3 mm × 5 m) columns. The error for reproducibility in conversion was ±4% and selectivity was less than ±5%.

3. Results and discussion

3.1. *Catalyst characterization*

The surface properties of the H-GaAlMFI zeolite used in this study are shown in Table 1. The H-GaAlMFI zeolite shows high acidity and presence of significant amount of non-framework Ga. High zeolitic acidity in combination with non-framework Ga-oxide species is crucial for high propane aromatization activity [11]. Our previous studies have demonstrated that the H-GaAlMFI zeolite is more active for the lower alkane aromatization process as compared to other Ga-based zeolites [12].

Table 1
Properties of H-GaAlMFI zeolite

Framework composition	Value
Si/Al	40.3
Si/Ga	49.9
Si/Al + Ga	22.3
Non-framework Ga (mmol/g)	0.32
Strong acidity[a]	0.46

[a] In terms of pyridine (mmol/g) chemisorbed at 400 °C.

3.2. *Effect of space velocity on propane conversion and product distribution*

Fig. 1 shows the effect of space velocity on the propane conversion at different temperatures. As expected the propane conversion increases with decreasing space velocity (increasing contact time) for the whole temperature range investigated. The effect of space velocity at 450, 500 and 600 °C on the product distribution for the propane aromatization reaction over H-GaAlMFI is shown in Fig. 2a–c, respectively. The following common trends in product selectivity are observed with decreasing space velocity/increasing propane conversion:

(a) Selectivity for propylene (C_3''), ethylene (C_2'') and butane/butylenes ($C_4 + C_4''$) decreases.
(b) Selectivity for methane (C_1) and ethane (C_2) increases.

However, the effect of space velocity on the aromatic (Ar) selectivity is also influenced by temperature. At 450 °C, the selectivity for aromatics continually increases with decreasing space velocity. However, at 500 and 600 °C, it appears to pass through a maxima; the effect is more pronounced at 600 °C. In case of the Ga/HZSM-5 zeolites, the aromatics were observed to continually increase with decreasing space velocity [3].

The aromatization activity/selectivity for GAlMFI zeolites is known to be strongly influenced by their strong acidity and extra-

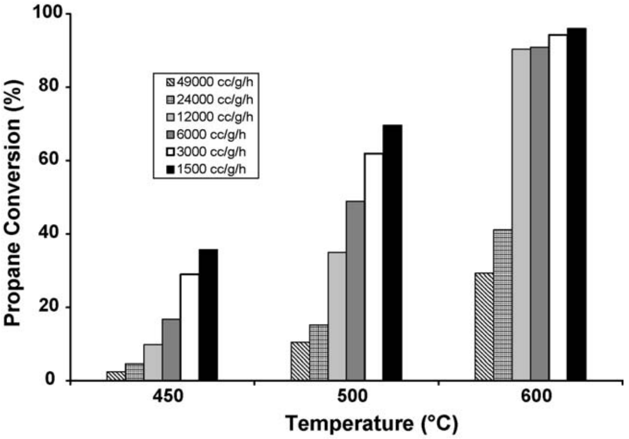

Fig. 1. Influence of space velocity (cm^3/g/h) on propane conversion at different temperatures.

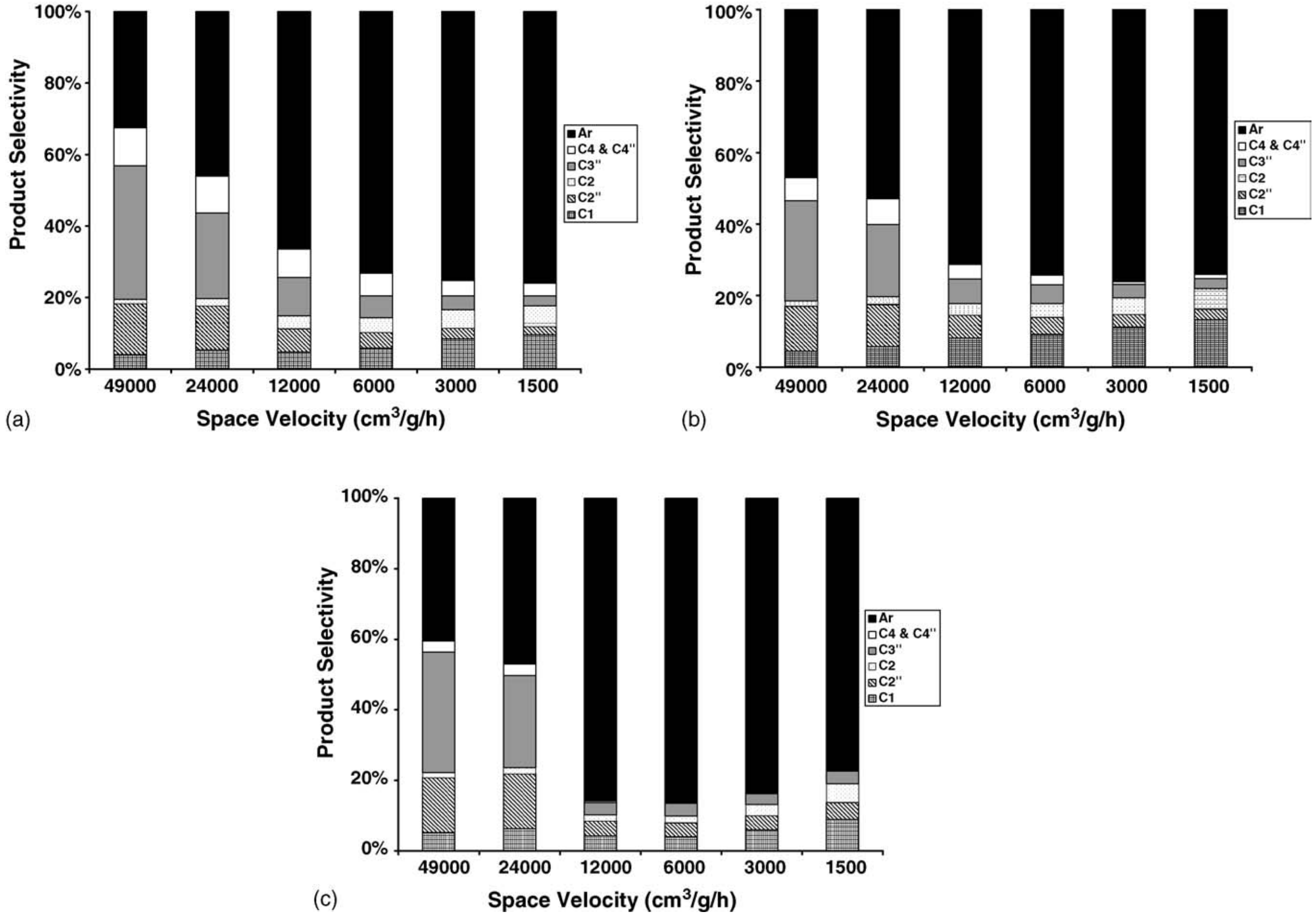

Fig. 2. Influence of space velocity ($cm^3/g/h$) on the product distribution for the propane aromatization reaction over H-GaAlMFI zeolite at (a) 450 °C, (b) 500 °C and (c) 600 °C.

framework (FW) Ga content [16]. It is therefore interesting to study the effect of space velocity on the propane conversion and product selectivity for a GaAlMFI zeolite with different strong acidity and extra-FW Ga content. In order to obtain such a zeolite the GAlMFI catalyst was calcined at a higher temperature (700 °C). The higher temperature calcined zeolite had considerably lower strong acidity (0.19 mmol/g) than the zeolite calcined at 600 °C (properties of the 600 °C calcined zeolite are shown in Table 1). Furthermore, it also had a different FW Si/Ga ratio (63.7) and thereby a different extra-FW content. In spite of these differences, the higher temperature calcined zeolite showed a similar trend (to that of the 600 °C calcined zeolite) for the effect of space velocity on the propane conversion (Fig. 3) and product selectivity (Fig. 4a and b) at the reaction temperature of 500 °C.

3.3. Effect of space velocity on A/C ratio

In case of the propane aromatization reaction it is desirable to maximize the aromatization/cracking (A/C) ratio. The A/C ratio is calculated as follows:

$$\frac{A}{C} = \left[\frac{\text{selectivity for aromatics}}{\text{selectivity for } C_1, C_2 \text{ and } C_2''}\right]$$

The A/C ratio is plotted as a function of space velocity at 450, 500 and 600 °C in Fig. 5. At all the three temperatures, the A/C ratio passes through a maximum with increasing space velocity. The maximum is observed in, more or less, the same space velocity range (5000–12,000 $cm^3/g/h$) for all the three temperatures. However, it should be noted that the conversion is considerably

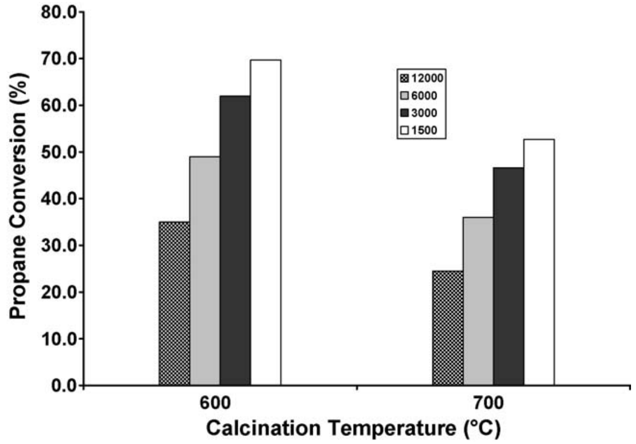

Fig. 3. Comparison of the influence of space velocity ($cm^3/g/h$) on propane conversion at 500 °C over the H-GaAlMFI zeolite calcined at 600 and 700 °C.

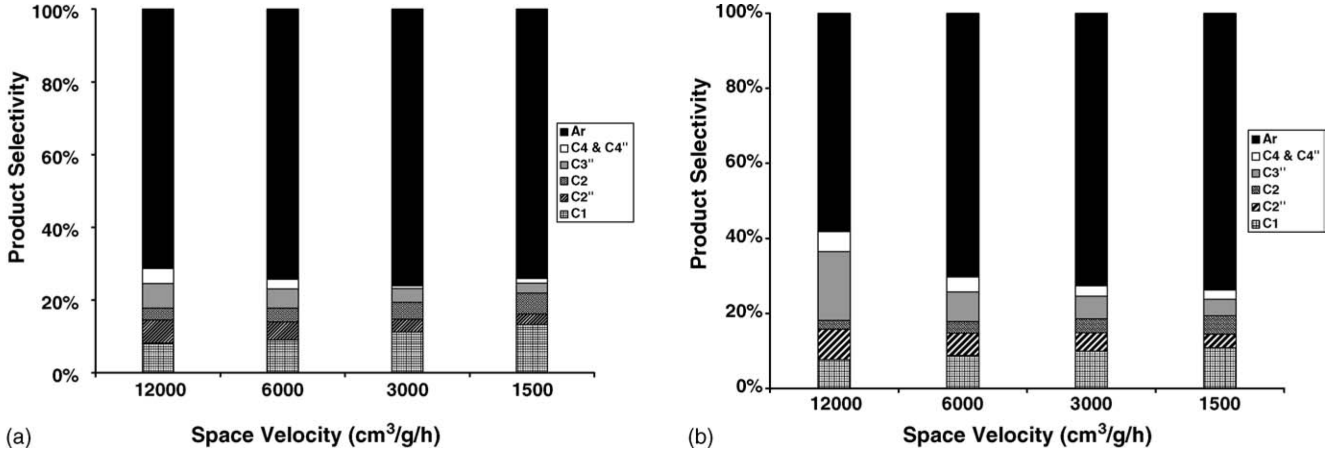

Fig. 4. Influence of space velocity (cm^3/g/h) on product selectivity at 500 °C over the H-GaAlMFI zeolite calcined at (a) 600 °C and (b) 700 °C.

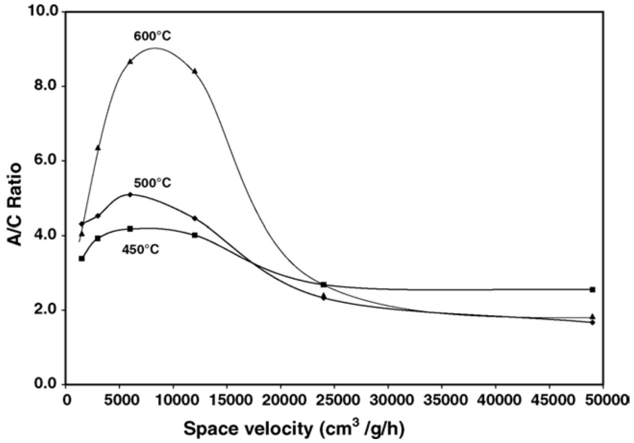

Fig. 5. Influence of space velocity (cm^3/g/h) on the aromatization/cracking (A/C) ratio at different temperatures.

different at similar space velocities at different temperature; for example the propane conversion is 17% at 450 °C and 90% at 600 °C at the space velocity (6000 cm^3/h/g) corresponding to the maximum in the A/C ratio. This suggests that the contact time determines the extent of aromatization and cracking for the propane aromatization reaction over H-GaAlMFI zeolite.

3.4. Effect of space velocity on aromatic distribution

Fig. 6a and b show the distribution of aromatic compounds as a function of aromatic yield (decreasing space velocity) at 450 and 600 °C. The aromatic distribution at 500 °C is similar to that observed at 450 °C and is not shown. The following common trends in product selectivity are observed with increasing aromatic yield/decreasing space velocity:

(a) Selectivity for toluene (T) increases.
(b) Selectivity for C_8 and C_9 aromatic compounds pass through a maximum; the concentration of C_8 species is significantly higher at the lower propane aromatization temperatures.

At the lower reaction temperatures, the selectivity for benzene (B) decreases considerably with initial increase in aromatic yield and then stabilizes. However, at 600 °C, the selectivity for benzene is found to decreases continually with increasing aromatic yields. Overall the general dependence of aromatic distribution on space velocity is similar for aromatization of propylene on H-ZSM-5 [17] and propane on H-GaMFI [13]; however, it is considerably different from that observed in propane aromatization over Pt/H-ZSM-5 [17], Zn/ZSM-11 [18] and Ga/H-ZSM-5

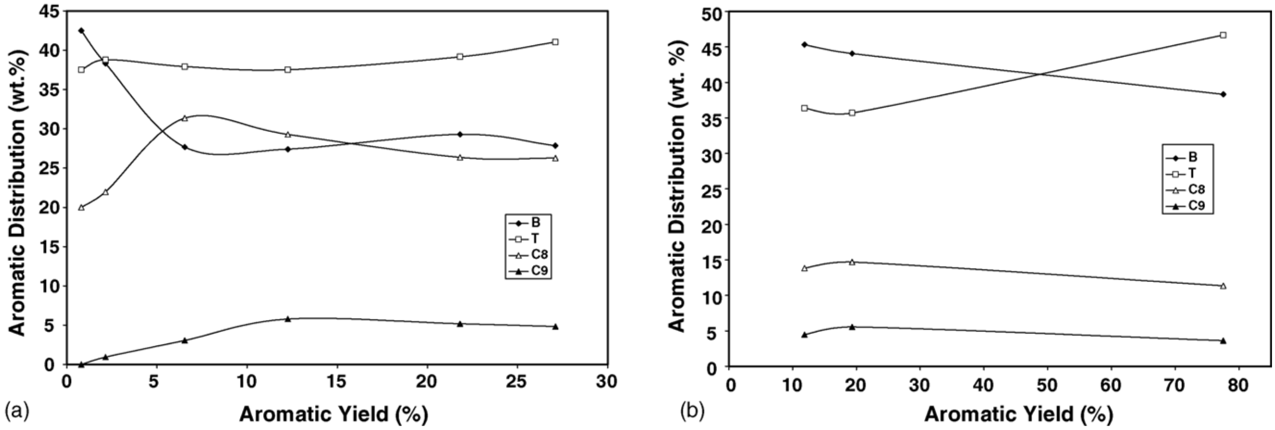

Fig. 6. Aromatic distribution as a function of aromatic yield (space velocity) at (a) 450 °C and (b) 600 °C.

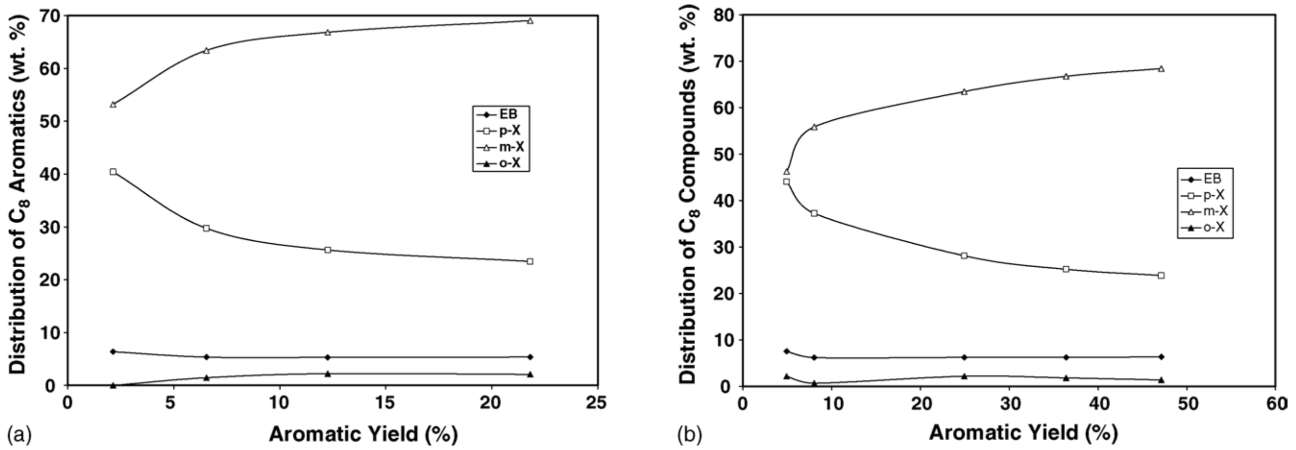

Fig. 7. Distribution of C_8 aromatics as a function of aromatic yield (space velocity) at (a) 450 °C and (b) 600 °C.

[3]. In case of propane aromatization over the Ga/H-ZSM-5 zeolite [3], the selectivity for benzene increased while that for toluene decreased with increasing aromatic yields.

Fig. 7 shows the distribution of C_8 aromatic compounds as a function of aromatic yield (decreasing space velocity) at 450 and 600 °C. While there is a decrease in the *p*-xylene (*p*-X) selectivity, there is a considerable increase in the selectivity for *m*-xylene (*m*-X) with increasing aromatic yields. There is no significant change in the concentration of ethyl benzene (EB). Concentrations of *o*-xylene were observed to be very small at all the temperatures. The *p*-X/*o*-X equilibrium ratio is expected to be 0.87 at 600 °C. This study shows that the *p*-X/*o*-X ratio far exceeds the thermodynamic equilibrium values under all process conditions. The *p*-X/*m*-X values were also observed to exceed the thermodynamic *p*-X/*m*-X value (0.454 at 600 °C) under certain process conditions. This is in line with our previous studies, wherein we observed that the distribution of xylene isomers in the propane aromatization reaction over H-GaAlMFI is kinetically controlled and not by reaction thermodynamics [14].

3.5. Reaction pathway

Fig. 8 shows the $C_2H_4/(CH_4\text{-}C_2H_6)$ molar ratio as a function of space velocity at 450 and 600 °C. Methane, ethane and ethane are the products of the following primary propane conversion reactions:

$$C_3H_8 \rightarrow CH_4 + C_2H_4$$

$$C_3H_8 + H_2 \rightarrow CH_4 + C_2H_6$$

Based on the stoichiometry of these reactions and considering that part of ethylene is further converted to higher hydrocarbons, the $C_2H_4/(CH_4–C_2H_6)$ molar ratio is always expected to be less than unity. However, the $C_2H_4/(CH_4–C_2H_6)$ molar ratio is observed to exceed unity under certain process conditions. This suggests that ethylene is not only formed by the cracking of propane but also via the cracking of higher hydrocarbons; for example from cracking of C_6 and C_9 alkenes, which are formed by dimerization and trimerization of propylene, respectively. This is also consistent with the appreciable selectivity observed for C_4 hydrocarbons (Fig. 2).

The observed decrease in the propylene selectivity and corresponding increase in aromatics yield at all temperatures (Fig. 2) is consistent with the fact that propylene is the primary intermediate product or one of the primary products in the aromatization process. A simplistic reaction pathway based on the product selectivity and aromatic distribution is shown in Fig. 9. Benzene, *p*-xylene, ethyl benzene are formed by direct aromatization (dehydrocyclization followed by dehydrogenation). C_9 aromatic compounds, *m*-xylene, *o*-xylene are formed by secondary reactions. Toluene is formed as a primary aromatic product as well as from secondary transformations depending on the space velocity. Formation of C_{9+} aromatics cannot be a primary process, due to the large steric hindrance expected in the ZSM-5 type zeolite channels for the bulky highly-substituted cycloalkane intermediates. However, secondary transformations of the more compact planar benzene nucleus (smaller aromatic compounds such as benzene, toluene and *p*-xylene formed by the primary process) may result in formation of C_{9+} aromatics [13]. The distribution of aromatics is controlled by both the direct aromatization and secondary transformation reactions depending on the

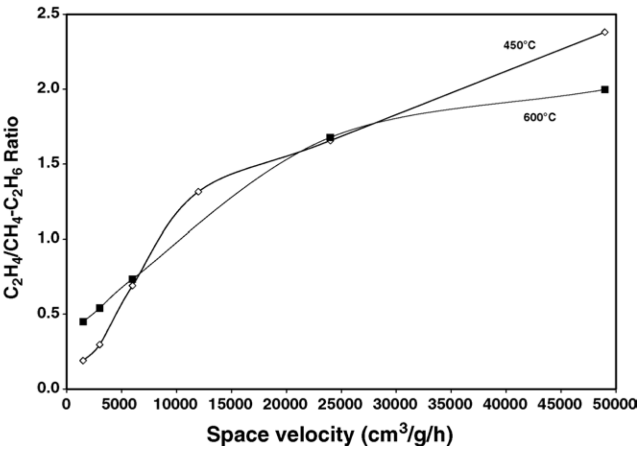

Fig. 8. Influence of space velocity ($cm^3/g/h$) on the $C_2H_4/(CH_4–C_2H_6)$ molar ratio.

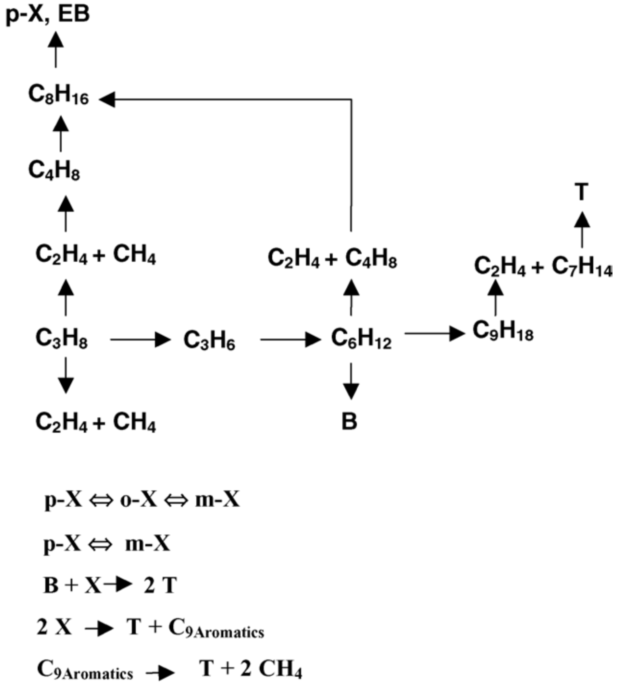

Fig. 9. Simplistic schematic of the propane aromatization reaction pathway over H-GaAlMFI.

contact time. The oligomerization, cracking, dehydrocyclization involving hydrogen transfer reactions are catalyzed by zeolitic proton acid sites (attributed to framework Al and Ga), while the dehydrocyclization involving dehydrogenation reactions are catalyzed by extra framework Ga species in combination with zeolitic protons.

4. Conclusions

The salient features of the study are summarized below:

(a) Space velocity/propane conversion was found to have a profound influence on the product selectivity and aromatic distribution.

(b) Selectivity for propylene, ethylene and C_4 hydrocarbons decreased, while that for methane and ethane increased with decreasing space velocity/increasing propane conversion. While the selectivity for aromatics continually increased with decreasing space velocity for lower temperature cases, it passed through a maximum for the high temperature case (600 °C).

(c) In the temperature range investigated, the aromatization/cracking ratio passed through a maximum with increasing space velocity; maximum aromatization/cracking ratio was observed in the space velocity range of 5000–12,000 $cm^3/g/h$

(d) Selectivity for toluene increased, while that for benzene decreased with increasing aromatic yields. Selectivity for C_8 and C_9 aromatic compounds passed through a maximum with increasing aromatic yields.

(e) The *p*-xylene selectivity decreased with increasing aromatic yields, while *m*-xylene selectivity increased. The selectivity for ethyl benzene did not alter significantly.

(f) A simplified reaction pathway was proposed based on the observed product distribution. Propylene was found to be the primary product for the aromatization reaction. Ethene was formed by the primary cracking of propane as well as from cracking of higher olefins. *p*-Xylene, benzene and ethyl benzene were the primary aromatic products, while *m*-xylene, *o*-xylene and C_9 compounds were formed via secondary transformations. Toluene is formed as a primary aromatic product and from secondary transformations.

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