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RESEARCH NOTE

Influence of Space Velocity on Product Selectivity and Distribution of Aromatics and Xylenes in Propane Aromatization over H-GaMFI Zeolite

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Aromatization of lower (C_3 and C_4) alkanes over Ga-modified ZSM-5 type zeolites (1–3) is a process of great practical importance. Earlier studies on the aromatization of propane over Ga_2O_3/H-ZSM-5 (4, 5) and H-GaMFI (6, 7) zeolites showed that the product selectivity in the process (at about 550°C) is strongly influenced by the conversion (i.e., by the space velocity or contact time). Although propane aromatization over different Ga-modified ZSM-5 type zeolites has been studied extensively during the past decade, studies covering the influence of space velocity (or contact time) on the product selectivity, particularly at different temperatures are scarce. It is also interesting to know the influence of space velocity on the distribution of aromatics and xylene isomers formed in the process at different temperatures. However, information on this is also very scarce.

In our earlier studies, H-GaMFI zeolite showed high activity and selectivity in the propane aromatization at 550°C (7–10); the aromatics selectivity in this process is increased significantly by increasing the conversion. The present investigation was undertaken with the objectives of studying at different temperatures the influence of space velocity on the selectivity to various products (viz., aromatics, methane, ethane, ethylene, propylene, and C_4 and C_{5+} aliphatics) and also on the distribution of aromatics and xylene isomers formed in the process for knowing the reaction path for the formation of aromatics and xylenes.

H-GaMFI zeolite (bulk Si/Ga = 39.5, framework Si/Ga = 53, Na/Ga = 0.03, and crystal size = 14 μm) was obtained by deammoniation of its NH_4 form at 600°C for 4 h in a flow of moisture-free N_2 (1800 $cm^3 \cdot g^{-1} \cdot h^{-1}$). The zeolite was prepared and characterized by the methods similar to that described earlier (7). The number of strong acid sites on the zeolite (measured in terms of the pyridine chemisorbed at 400°C) were 0.25 $mmol \cdot g^{-1}$. Propane aromatization reaction over the zeolite catalyst was carried out at atmospheric pressure in a continuous flow quartz reactor (13 mm ID) provided with a Chromel-Alumel thermocouple in the center of the catalyst bed (containing 1 g catalyst), using a propane–nitrogen mixture (50 mol% propane) as a feed. The conversion and selectivity data at different space velocities (400–155,000 $cm^3 \cdot g^{-1} \cdot h^{-1}$) and temperatures (425–600°C) in the absence of catalyst deactivation (i.e., initial activity/selectivity) were obtained by a 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 reactant mixture be 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), Benton-34 (5%), and dinonylphthalate (5%) on Chromosorb-W (3 mm × 5 m) columns.

Results in Figs. 1 and 2 show a strong influence of the space velocity on the propane conversion and product selectivity in the propane aromatization at the different temperatures (425–600°C). Hence, the results also indicate a strong dependence of the selectivity on the propane conversion. When the space velocity is increased (or the conversion is decreased) the selectivity for aromatics is increased markedly, whereas that for propylene is increased at all the temperatures. However, the selectivity for ethylene and C_4 hydrocarbons is increased at lower temperatures and is passed through a maximum at higher temperatures. There was no formation of C_{5+} aliphatics at any temperature. The observed decrease in the propylene selectivity and increase in the aromatics selectivity with increasing the conversion is consistent with the fact that propylene is the primary intermediate product or one of the primary products in the aromatization process (1–3).

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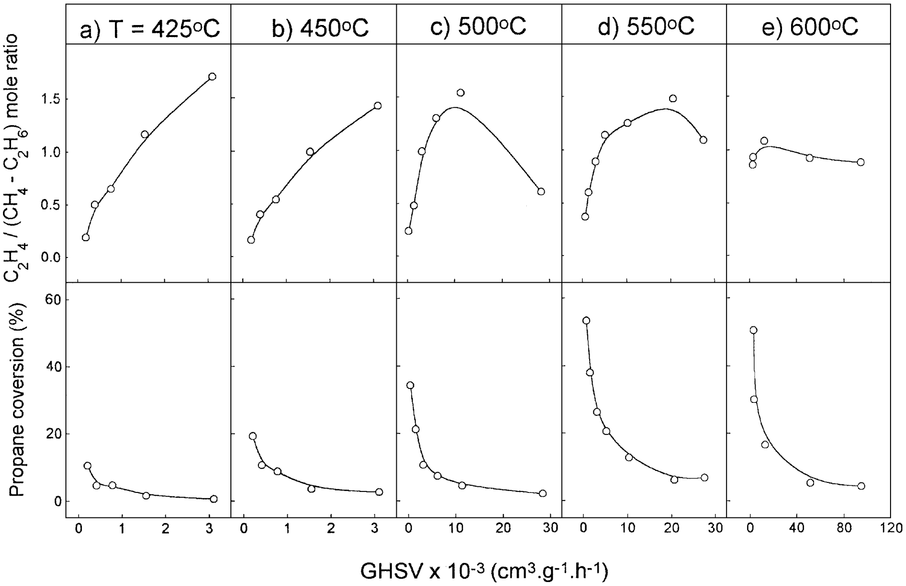

FIG. 1. Effect of space velocity on the conversion and moles of C_2H_4/(moles of CH_4 minus moles of C_2H_6) ratio in the propane aromatization at different temperatures.

The methane, ethane, and ethylene are primary products of the following propane conversion reactions:

$$C_3H_8 \xrightarrow{H^+} CH_4 + C_2H_4 \quad [1]$$

$$C_3H_8 + H_2 \xrightarrow{H^+} CH_4 + C_2H_6 \quad [2]$$

According to the stoichiometry of these reactions and considering that a part of the ethylene is converted to higher hydrocarbons, the moles of C_2H_4/(moles of CH_4 minus moles of C_2H_6) ratio is expected to be always less than 1. However, under certain conditions, the ratio is even more than 1 (Fig. 1). This observation indicates that ethylene is formed not only by the cracking of propane (reaction 1) but also by the cracking of higher hydrocarbons viz., C_6 and C_9 alkenes formed by dimerization and trimerization of propylene. The observed appreciable selectivity for C_4 hydrocarbons (Fig. 2) is consistent with this.

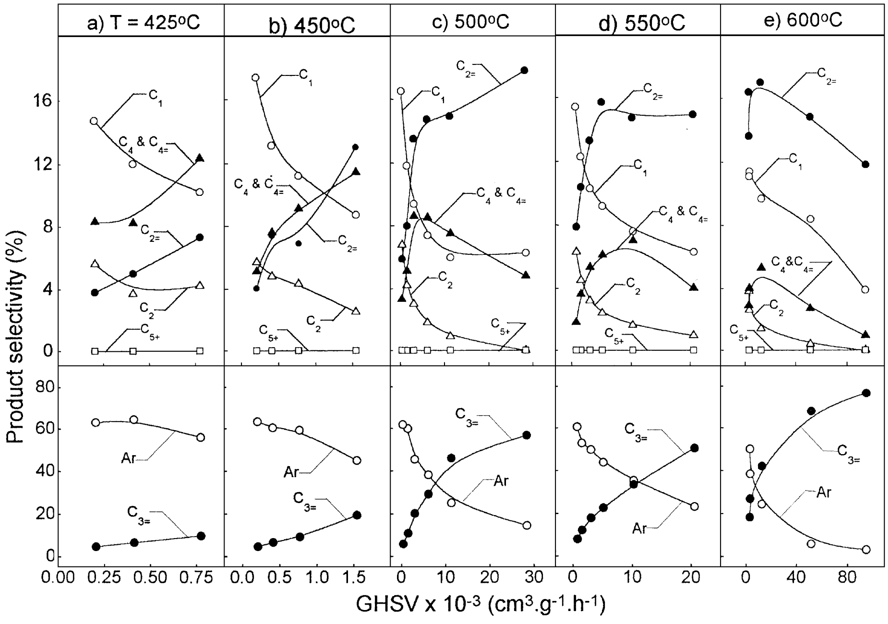

FIG. 2. Effect of space velocity on product selectivity in the propane aromatization at different temperatures.

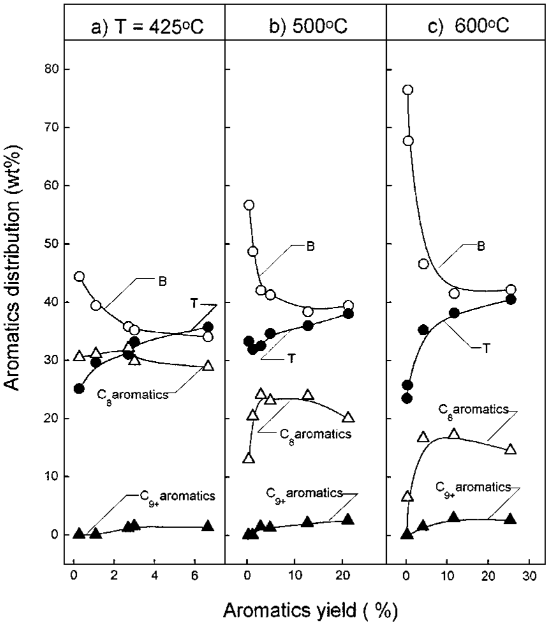

FIG. 3. Dependence of aromatics distribution on the aromatics yield in the propane aromatization at different temperatures.

Dependence of the aromatics distribution on the aromatics yield in the propane aromatization at the different temperatures is presented in Fig. 3. The aromatics distribution is strongly influenced by the extent of aromatization, particularly at the lower aromatics yield. With the increase in the aromatics yield, the formation of benzene relative to that of the higher aromatics is decreased very significantly, the relative formation of toluene and C_{9+} aromatics is increased and that of C_8 aromatics passes through a maximum. It is interesting to note that the dependence of aromatics distribution on the space velocity or aromatics yield is quite different from that observed in the aromatization of propane over PtH-ZSM-5 (11), Zn/ZSM-11 (12), and Ga/H-ZSM-5 (3) catalysts at 530–540°C. In the present case, the trends observed for benzene, toluene, and xylenes are, however, quite similar to those observed earlier in the aromatization of propylene over H-ZSM-5 (11).

Figure 4 shows that the xylene distribution is very strongly influenced by the xylenes yield (or space velocity) and reaction temperature. At all temperatures, when the xylenes yield is increased, the relative concentration of *p*-xylene in xylenes is sharply decreased, whereas that of *m*-xylene is sharply increased. The relative concentration of *o*-xylene is also increased but to a small extent. The formation of *o*-xylene relative to that of other xylene isomers is very small. A comparison of the high and low temperatures (425 and 600°C) results indicates that, for the same xylenes yield, the *p*-X/*m*-X ratio at the higher temperature is much higher than that at the lower temperature. This is most probably because of the fact that, for obtaining the same xylenes yield, the contact time at the lower temperature is much higher than that at the higher temperature. During the larger contact time at the lower temperature, *p*-xylene can undergo isomerization to *m*-xylene and *o*-xylene, thus approaching the equilibrium concentration of xylenes. Nevertheless, the results show that *p*-xylene is a primary product among the xylenes formed in the propane aromatization. The xylenes distribution results from the isomerization of *p*-xylene to *m*- and *o*-xylenes, depending upon the temperature and space velocity (or contact time).

It may be noted that the formation of 1,2 or 1,3 dimethyl cyclohexane over 1,4 dimethyl cyclohexane in the channels of ZSM-5 type zeolite is not favored because of a very high steric hindrance involved in the formation of the former molecules during the dehydrocyclization of C_8 alkene. For the same reason, the formation of higher alkyl cyclohexane and hence, the trimethyl and tetra methyl benzenes directly from C_9 and C_{10} alkenes, respectively, in the zeolite channels is highly sterically hindered and therefore not possible. However, after the aromatization (i.e., after the formation of the benzene nucleus, which is planar and smaller in size), the steric hindrance is reduced, making possible the secondary aromatics transformation reactions, such as isomerization, disproportionation and alkylation/dealkylation reactions.

Thus, based on the above observations for the formation of ethylene both from propane and higher hydrocarbons (viz., C_6 and C_9 alkenes) and the distribution of aromatics and xylenes, a possible reaction path for the formation of different aromatics in the propane aromatization process

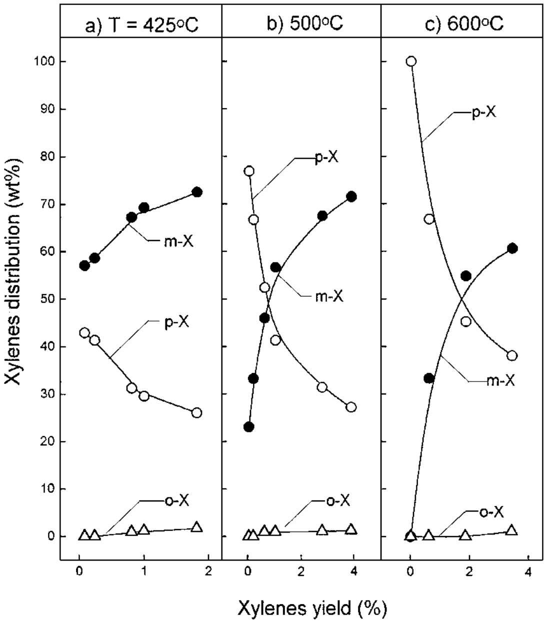

FIG. 4. Dependence of xylenes distribution on the xylenes yield in the propane aromatization at different temperatures.

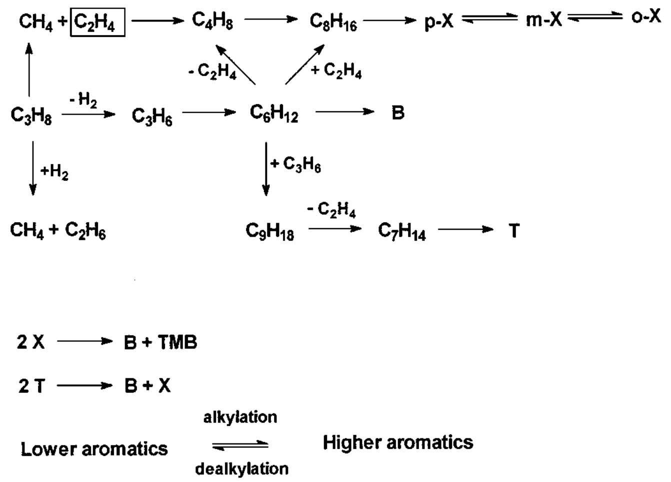

FIG. 5. Reaction path for the formation of different aromatics in the aromatization of propane (B = benzene, T = toluene, X = xylene, TMB = trimethyl benzene).

over H-GaMFI zeolite catalyst is proposed, as presented in Fig. 5. As discussed earlier, benzene, toluene, and *p*-xylene are formed from the direct aromatization reaction whereas, other aromatics are formed by the secondary aromatics transformation reactions—isomerization of *p*-xylene to *m*-xylene and then *m*-xylene to *o*-xylene, disproportionation of xylenes to toluene and trimethyl benzenes, and alkylation of lower aromatics to higher aromatics. Also, the disproportionation of toluene to benzene and xylenes, and dealkylation of alkyl benzenes are also expected to occur in the overall process.

This investigation leads to the following important conclusions. The product selectivity in propane aromatization over H-GaMFI zeolite catalyst is very strongly influenced by the space velocity and consequently by the conversion. The distribution of aromatics and xylene isomers is also very strongly influenced by the yield of aromatics and xylenes, respectively, in the aromatization process and also by the temperature. Ethylene is formed in the process not only by propane cracking but also by the cracking of higher hydrocarbons. Benzene, toluene and *p*-xylene are formed by direct aromatization (i.e., dehydrocyclization followed by dehydrogenation), but the other aromatics result from the secondary aromatics transformation reactions. The distribution of aromatics and xylene isomers is controlled by both the direct aromatization and the secondary aromatics transformation reactions, depending upon the contact time.

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