Simultaneous aromatization of propane and higher alkanes or alkenes over H-GaAlMFI zeolite

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Conversion of propane in its aromatization over H-GaAlMFI zeolite can be enhanced by a factor of about two by carrying out the aromatization simultaneously with that of higher alkanes or alkenes; this is mostly due to hydrogen-transfer reactions between propane and higher alkenes.

Aromatization of propane or lower alkanes over Ga-modified ZSM-5 type zeolites is a process of great practical importance.[1-3] The high aromatization activity of these zeolites is attributed to their bifunctional activity, high dehydrogenation function due to the presence of extraframework Ga–oxide species (in combination with zeolitic protons) and high acidity due to the framework Al and/or Ga. Among the zeolites (Ga/H-ZSM-5, H-GaMFI and H-GaAlMFI), H-GaAlMFI zeolite shows the highest activity/selectivity in the aromatization of alkanes.[4,5] This is because of the uniform distribution and/or high dispersion of the extraframework Ga–oxide species in the channels, resulting from the removal of framework Ga during the calcination and/or pretreatment of the zeolite. We show here that the conversion of propane in its aromatization over H-GaAlMFI zeolite is enhanced to a large extent when the aromatization of propane is carried out simultaneously with that of alkenes or higher alkanes. Because of this, propane can be converted into aromatics with high conversion, even at low temperatures.

H-GaAlMFI (H-galloaluminosilicate of ZSM-5 type) zeolite, having framework (FW) Si/Ga of 49.9, FW Si/Al of 40.3 (with no non-FW Al), Na/(Ga + Al) of 0.03, non-FW Ga of 0.32 mmol g^{-1}, spherical–hexagonal crystals of 5.5 ± 1.5 μm size and 0.46 mmol g^{-1} strong acid sites (measured in terms of the amount of pyridine chemisorbed at 400 °C), was prepared and characterized by procedures similar to those described elsewhere.[5] The propane aromatization reaction was carried out in a continuous tubular quartz flow reactor (i.d. 13 mm) by passing a mixture of propane (> 99.95%), with or without added alkene or higher alkane, over the zeolite catalyst (0.5 g), using a square pulse technique. The feed and product streams were analysed by an on-line GC. The carbon balance across the reactor was within 2–5% error. Detailed experimental procedures have been described previously.[6]

Results showing an enhancement in propane aromatization over the zeolite due to the presence of various alkenes or higher alkanes are presented in Table 1. The enhancement is quite large, being about twofold. The selectivity in the simultaneous aromatization of propane and higher alkanes (or alkenes) is higher than that for propane alone. The product distributions in the individual experiments (Table 1) are given in Table 2.

The observed enhancement in propane conversion (Table 1) can be explained by a hydrogen-transfer reaction between propane and higher alkenes [eqn. (1)] giving propene and a

$$C_3H_8 + C_nH_{2n} \rightarrow C_3H_6 + C_nH_{2n+2}\ (n > 3) \qquad (1)$$

higher alkane. Since the higher alkane has a higher reactivity than propane, it undergoes dehydrogenation faster [eqn. (2)].

$$C_nH_{2n+2} \xrightarrow{\text{H}^+ \text{ and Ga–oxide}} C_nH_{2n} + H_2 \qquad (2)$$

The propene and higher alkene then undergo oligomerization and dehydrocyclization or aromatization reactions [eqn. (3)].

$$C_nH_{2n} \xrightarrow{\text{H}^+} C_6\text{–}C_{10}\ \text{alkenes} \xrightarrow{\text{H}^+ + \text{Ga–oxide}} \text{aromatics} \qquad (3)$$

The enhancement observed in the presence of higher alkanes also involves the above reactions but in the sequence (2), (1), (2), (3). However, the enhancement due to ethene is expected to be caused by the hydrogen-transfer reaction between propane and butene formed by dimerization of ethene. Thus, the enhancement involves internal recycling of higher alkenes or alkanes (which have higher reactivity than propane) in the

Table 2 Product distribution in the individual experiments of Table 1

Product distribution (mass %)	Experiment no. 1	2	3	4	5	6	7
CH_4	1.1	1.1	0.5	0.8	1.8	0.5	1.0
C_2H_4	0.8	0.9	1.2	0.7	1.5	0.7	2.0
C_2H_6	0.7	1.3	0.8	0.6	1.6	0.3	1.1
C_3H_6	1.1	0.0	1.8	0.8	2.0	1.1	3.1
C_3H_8	85.7	43.4	42.4	43.0	39.6	93.0	44.1
C_4H_8	0.0	0.0	4.2	0.0	0.0	0.0	0.0
C_4H_{10}	1.2	2.4	2.5	3.1	6.5	0.6	8.1
C_{5+} aliphatics	0.0	0.0	0.0	0.0	2.7	0.0	17.1
Benzene	3.2	6.9	3.8	4.7	4.4	1.4	2.8
Toluene	3.4	22.6	17.7	23.2	15.6	1.4	8.8
Ethylbenzene + xylenes	2.3	17.8	21.0	20.0	20.3	0.9	9.8
C_{9+} aromatics	0.5	3.6	4.1	3.1	4.0	0.1	2.1

Table 1 Results of the simultaneous aromatization of propane and alkenes or higher alkanes over H-GaAlMFI zeolite at 450 °C

Expt. no.	Reactant (A) other than propane	A/C_3H_8 mole ratio	Space velocity/ $cm^3\ g^{-1}\ h^{-1}$	Conversion (%) Propane	A	Aromatics selectivity (%)
1	—	0.0	6200	14.3	—	65.5
2	Ethene	1.0	6200	27.5	97.8	91.4
3	*n*-Butene	0.6	6200	25.0	90.4	87.6
4	Isobutene	0.5	6200	31.1	100	89.5
5	*n*-Hexane	0.5	6200	23.1	94.5	76.7
6	—	0.0	12400	7.0	—	54.3
7	*n*-Hexane	0.5	12400	12.1	65.7	60.5

catalytic process, resulting in faster conversion of propane to propene (by the hydrogen-transfer reactions) relative to the dehydrogenation of propane (which is a limiting step in propane aromatization[1]). Further detailed studies are necessary to more fully understand the hydrogen-transfer reactions over the bifunctional zeolite catalyst.

In summary, by carrying out propane aromatization simultaneously with alkene or higher alkane aromatization over H-GaAlMFI, propane conversion can be enhanced to a large extent and/or propane can be converted into aromatics with high conversion even at low temperatures. This has significant practical implications.

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Footnote

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