Methane transformation into aromatic hydrocarbons by activation with LPG over Zn-ZSM-11 zeolite

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Methane (C_1) can be activated by interaction with liquefied petroleum gas (LPG) even at very high C_1 molar fractions in the feed ($C_1/(C_1 + \text{LPG}) = 0.85$) at temperatures of 450–550 °C, GHSV(LPG) $= 2240$ and 810 ml/g h, over Zn-ZSM-11 (molar fraction $Zn^{2+}/(Zn^{2+} + H^+) = 0.86$) and total pressure of 1 atm. The isobutane (i-C_4) of LPG could be the main responsible of this interaction. Aromatic hydrocarbons were the main products in the whole range of C_1 molar fractions (0.4–0.85) studied, reaching excellent levels of 10–45%.

Keywords: methane activation, LPG, aromatic hydrocarbons, Zn-zeolite

1. Introduction

One way to increase the value of low cost liquefied petroleum gas (LPG) cut from petroleum feedstocks is its direct transformation into hydrogen (H_2) and into valuable aromatics (mainly benzene (B), toluene (T) and C_8 aromatics (X)) [1–3]. These aromatic products (BTX) have two main industrial uses: as a blending mixture to enhance the octane number of gasoline, even if due to antipollution legislations their utilization tends to decrease [4], and as a raw material for the petrochemical industry. Aromatic chemicals represent about 30% of the total 8 million known organic compounds [5].

Light hydrocarbons are becoming an attractive feed for the production of aromatics. Indeed, production regions of LPG are in many cases far away from consumption centres with a consequent high cost for transportation. This is why various companies have looked for ways of converting LPG into more valuable products. In particular, the Cyclar process using a gallium-loaded zeolite has been developed for converting LPG into aromatics [6,7]. The ZSM-5 and ZSM-11 zeolites are currently of particular interest as catalysts for the aromatization of light paraffins. Modifications of zeolites with zinc or gallium have been successfully used for this purpose [8–13]. We have reported that Zn-ZSM-11 shows excellent aromatization behavior for ethane (C_2), propane (C_3), liquefied petroleum gas (LPG), and pentane (C_5) [14–17].

Direct conversion of methane (C_1) to more valuable compounds, such as liquid hydrocarbons, is not only a promising approach for the utilization of natural gas (NG) resource but also a challenging technical project. C_1 (the main compound of NG) conversion, under non-oxidizing conditions, is a great task to catalysis science. Wang et al. [18] and Pierella et al. [19] reported the aromatization of C_1 in the presence of small amounts of light hydrocarbons under non-oxidizing conditions over Mo-zeolite at low pressures (1–2 atm). In our previous paper [20], we described the transformation of methane into aromatic hydrocarbons by activation with ethane over Zn-ZSM-11 zeolite. In this work, the transformation of pure LPG and the activation of methane with LPG using zinc-loaded ZSM-11 zeolite was studied.

2. Experimental

Catalytic reactions were carried out in a continuous flow quartz reactor with a 10 mm inner diameter at atmospheric pressure. Products were withdrawn periodically from the outlet of the reactor and analyzed by an on-line gas chromatograph equipped with a FID detector. The feeds used in this study were: high-purity methane (>99.97%) supplied by AGA and liquefied petroleum gas LPG (analysis: propane (C_3) $= 38.7$; isobutane (i-C_4) $= 36.3$; butane (C_4) $= 25$ mol%) supplied by YPF (Argentina). The studies with LPG were carried out at GHSV $= 2240$ and 810 ml/g h and 550 °C. The feed $C_1 + \text{LPG}$ with LPG molar fraction of 0.15 was evaluated at temperatures between 450 and 550 °C and GHSV(LPG) $= 2240$ and 810 ml/g h corresponding to GHSV(C_1) $= 12690$ and 4590 ml/g h, respectively. Also, the feed $C_1 + \text{LPG}$ was evaluated at different C_1 molar fractions between 0.4 and 0.85 corresponding to GHSV(C_1) between 540 and 4590 ml/g h, at constant GHSV(LPG) $=$ 810 ml/g h and 450 and 550 °C. The reaction products were analyzed using a 2 m Porapak Q column. Conversion and

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products distribution were expressed on a carbon-atom basis. The Zn-ZSM-11 catalyst (Si/Al = 17) with zinc molar fraction $Zn^{2+}/(Zn^{2+} + H^{+}) = 0.86$ was synthesized and characterized according to [21–23].

3. Results and discussion

The results of LPG and C_1 conversion and products distribution as a function of GHSV(LPG) at 550 °C, over Zn-ZSM-11 zeolite are summarized in table 1, using two different feeds, i.e., LPG and $LPG/(LPG + C_1) = 0.15$. When the feed was LPG, its total conversion and that of each individual component increased with decreasing GHSV(LPG). Also, as the GHSV(LPG) decreased, aromatics yield increased whereas $C_2^=$ yield decreased because it was introduced into the polymerization, cyclization, dehydrogenation and aromatization complex mechanisms. These results are consistent with those reported by Anunziata and Pierella [16]. These authors showed that the LPG conversion increased with the contact time (5–20 g h/mol) and then exhibited a modest increase whereas the aromatics yield reached through a maximum at contact time 18 g h/mol, at 540 °C using Zn-ZSM-11 zeolite. They also suggested that the zinc species caused an important effect on the LPG conversion, as well as on aromatics yield.

Thermodynamic data have shown that the conversion of paraffins into aromatics is favored by increasing the length of the chain [2]. As can be seen in table 1, the i-C_4 conversion is the highest, reaching levels higher than 98%. Then, i-C_4 appears as the more reactive LPG component, which would have the lowest activation energy to form the tertiary carbenium cation intermediates [3]. These findings would justify the following hydrocarbons conversion order when the feed was LPG: $i\text{-}C_4 > C_4 > C_3$. Furthermore, the C_3 and C_4 conversion increased significantly with decreasing GHSV(LPG), whereas the i-C_4 conversion showed a modest decrease when the feed was LPG. It can be suggested that the i-C_4 conversion approached nearly the equilibrium maximum levels under the reaction conditions studied. The equilibrium conversion of i-C_4 could be obtained at higher GHSV(LPG) than the equilibrium conversion of the other LPG components.

The LPG conversion decreased as its molar fraction decreased to $LPG/(LPG + C_1) = 0.15$ by adding C_1 to the feed. The C_3 and C_4 conversion approached nearly zero, which could be attributed to the low reactivity of these LPG components and their low partial pressures when the LPG molar fraction in the feed was $LPG/(LPG + C_1) = 0.15$. The C_1 and i-C_4 conversion increased as the GHSV(LPG) and GHSV(C_1) decreased. The i-C_4 conversion reached 89% and C_1 was activated rising to a conversion level of 6% at GHSV(LPG) = 810 ml/g h and 550 °C. We suggest that C_1 may be activated by i-C_4, initiating in this way its transformation [14,20]. When GHSV(LPG) and GHSV(C_1) decreased, the aromatics production was also favored.

Figure 1 shows the influence of temperature on the LPG ($C_3, C_4, i\text{-}C_4$) conversion at GHSV(LPG) = 810 ml/g h and LPG molar fraction in the feed $LPG/(LPG + C_1) = 0.15$, over Zn-ZSM-11. The i-C_4 conversion increased significantly with increasing temperature, whereas C_1 conversion showed a modest increase. C_3 and C_4 conversion remained nearly zero and increase of temperature failed to activate these LPG components. Then, the i-C_4 (LPG) transformation as well as the C_1 transformation by activation with i-C_4 (LPG) would be favored when the temperature increases.

Figure 2 shows the influence of temperature on the products distribution at GHSV(LPG) = 810 ml/g h and LPG molar fraction in the feed $LPG/(LPG + C_1) = 0.15$, over Zn-ZSM-11. The C_2 and C_5–C_6 yield remained very low

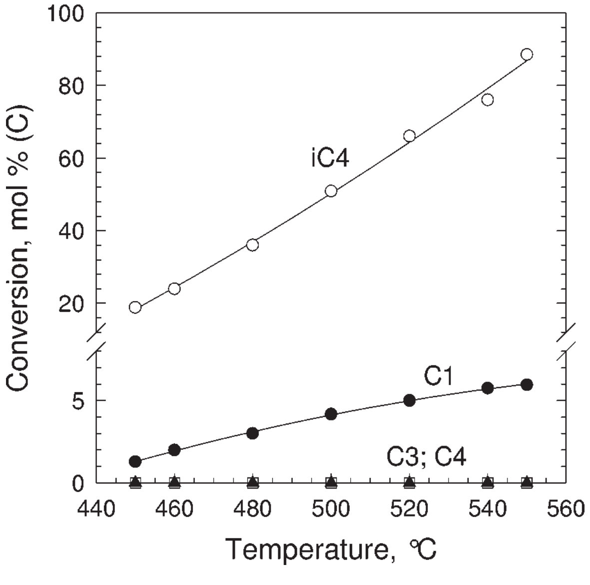

Figure 1. Influence of temperature on the LPG ($i\text{-}C_4, C_4, C_3$) and C_1 conversion over Zn-ZSM-11 catalyst. Feed: LPG + C_1, GHSV(LPG): 810 ml/g h, C_1 molar fraction: 0.15, total pressure: 1 atm.

Table 1
Reaction of LPG and LPG + C_1 feeds over Zn-ZSM-11 catalyst. Temperature: 550°C, total pressure: 1 atm.

Molar fraction LPG/(LPG + C_1)	GHSV(LPG) (ml/g h)	GHSV(C_1) (ml/g h)	Conversion (C) (mol%)				Products distribution (C) (mol%)		Products selectivity (C) (mol%)	
			C_1	C_3	i-C_4	C_4	$C_2^=$	HA	$C_2^=$	HA
1	2240	0	–	12.4	82.6	32.5	3.3	34.2	7.2	74.9
1	810	0	–	40.2	98.4	79.6	1.5	64.4	2.0	85.9
0.15	2240	12690	0.6	0.0	64.7	0.0	1.0	5.3	15.3	81.3
0.15	810	4590	6.0	0.0	88.5	0.0	2.1	12.0	14.4	82.5

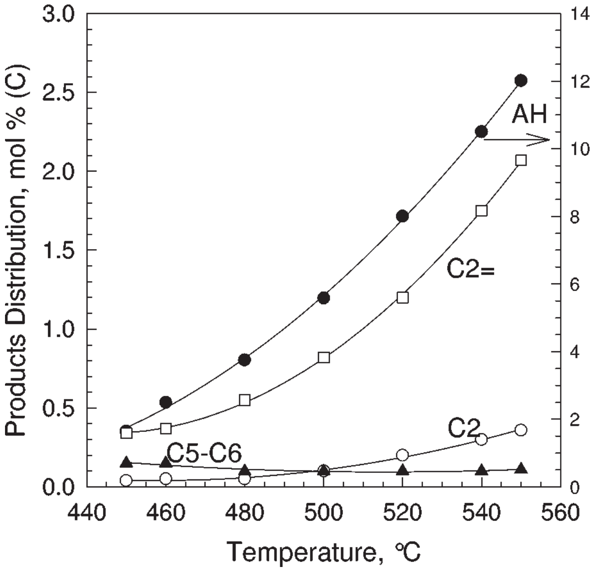

Figure 2. Influence of temperature on the reaction products distribution over Zn-ZSM-11 catalyst. Feed: LPG + C_1, GHSV(LPG): 810 ml/g h, C_1 molar fraction: 0.15, total pressure: 1 atm.

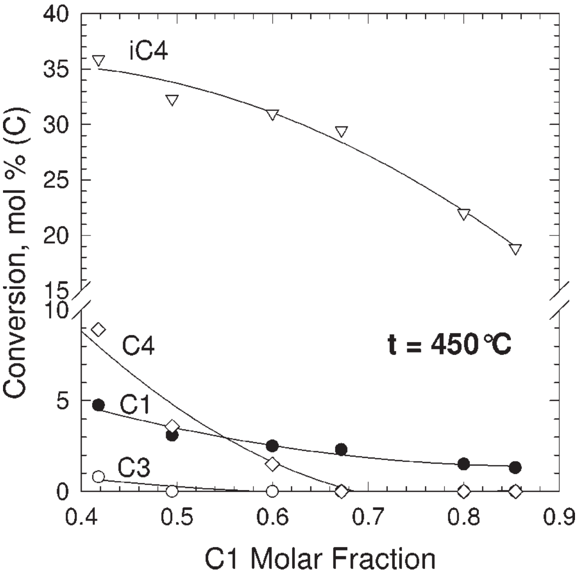

Figure 3. C_1 and LPG (C_3, C_4, i-C_4) conversion against the C_1 molar fraction over Zn-ZSM-11 catalyst. Feed: LPG+C_1, GHSV(LPG): 810 ml/g h, temperature: 450 °C, total pressure: 1 atm.

with the temperature increase whereas the $C_2^=$ and AH yield increased. Aromatic hydrocarbons were the main products in the whole range of temperatures studied, reaching a total of 12% at 550 °C. These products would arise from the simultaneous occurrence of the large number of reactions in the overall process of LPG transformation and C_1 activation.

The progress of the catalytic reactions of a gas mixture C_1 + LPG at GHSV(LPG) = 810 ml/g h, over Zn-ZSM-11 can be observed in figures 3 and 4. These figures show C_1 and LPG (C_3, C_4, i-C_4) conversion at different molar fractions of C_1 and temperatures of 450 and 550 °C, respectively. According to the data shown in these figures, C_1 and LPG conversion increased as the C_1 molar fraction decreased. At 550 °C, only C_4 conversion increased significantly with decreasing C_1 molar fraction, whereas C_1 and i-C_4 conversion showed a modest increase. At 450 °C, C_1 and i-C_4 conversion are more affected by a decrease of C_1 molar fraction than at 550 °C. Then, a direct relationship between the C_1 conversion and the i-C_4 conversion can be observed. We suggest that methane activation could occur through the interaction with i-C_4 (more reactive LPG component). The maximum C_1 conversion was nearly 10% at 550 °C, GHSV(LPG) = 810 ml/g h and C_1 molar fraction of 0.62. A decrease of C_1 molar fraction failed to increase C_1 conversion. It seems that the C_1 and i-C_4 conversion reached the maximum levels for the reaction system equilibrium under the experimental conditions studied. Furthermore, the numerous reactions involved in the complex reaction pathway of methane and LPG conversion can also produce methane, which would contribute to decreasing the neat conversion of this reactant. The strong Lewis acid sites present in Zn-zeolite [22,23], as EDA (electron-donor–acceptor) complex would allow the interaction of reactive intermediates with C_1 [14,24].

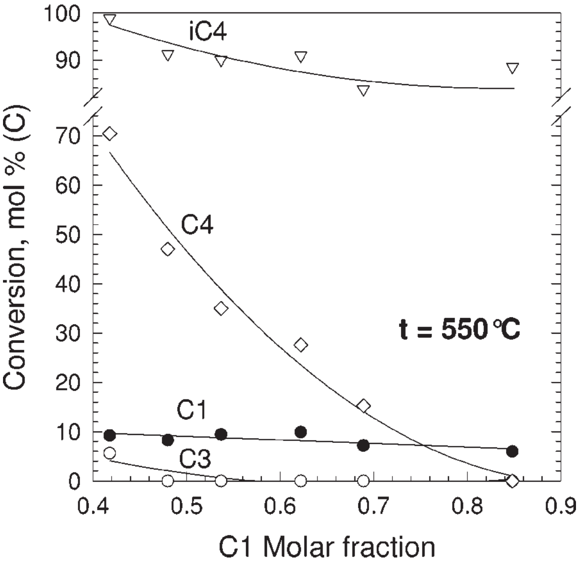

Figure 4. C_1 and LPG (C_3, C_4, i-C_4) conversion against the C_1 molar fraction over Zn-ZSM-11 catalyst. Feed: LPG+C_1, GHSV(LPG): 810 ml/g h, temperature: 550 °C, total pressure: 1 atm.

It can be seen in figure 4 that C_1 conversion is approximately 6% at a C_1 molar fraction as high as 0.85, when the feed was C_1 + LPG at 550 °C and GHSV(LPG) = 810 ml/g h, over Zn-ZSM-11. Taking into account [20], upon a C_1 molar fraction of 0.82, C_1 was not converted when the feed was C_1 + C_2 at 550 °C and GHSV(C_2) = 810 ml/g h, over Zn-ZSM-11. Thus, although C_2 is able to activate C_1 allowing excellent C_1 conversion levels at low C_1 molar fractions in the feed, the use of LPG as additive to the C_1 feed is able to activate it even at very high C_1 molar fractions in the feed.

Figures 5 and 6 show the products distribution as a function of C_1 molar fraction for a feed of C_1 + LPG over

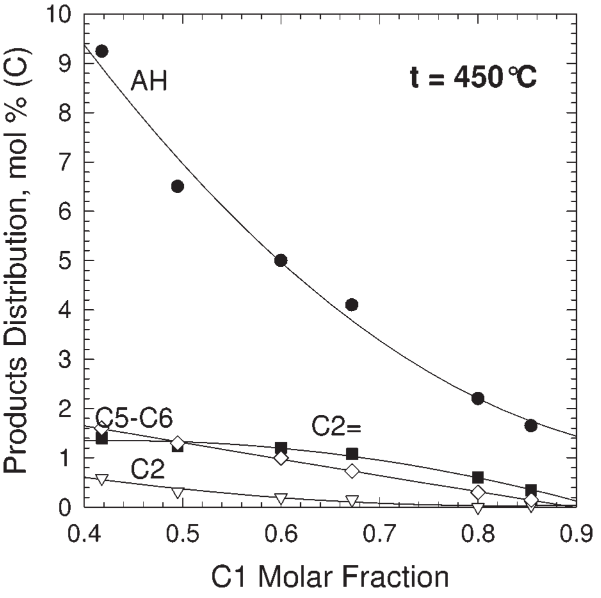

Figure 5. Reaction products distribution against the C_1 molar fraction over Zn-ZSM-11 catalyst. Feed: LPG + C_1, GHSV(LPG) = 810 ml/g h, temperature: 450 °C, total pressure: 1 atm.

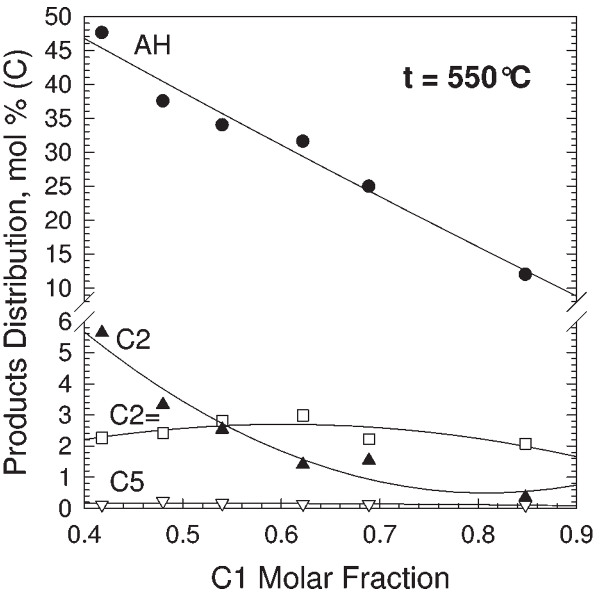

Figure 6. Reaction products distribution against the C_1 molar fraction over Zn-ZSM-11 catalyst. Feed: LPG + C_1, GHSV(LPG): 810 ml/g h, temperature: 550 °C, total pressure: 1 atm.

Zn-ZSM-11 at GHSV(LPG) = 810 ml/g h and 450 and 550 °C, respectively. As the C_1 molar fraction decreased, C_2, $C_2^=$, C_5 and C_6 yields increased slightly, whereas AH yield increased significantly. At 450 °C, the C_5–C_6 yield was higher than the C_2 yield but this was exactly the opposite at 550 °C. Thus, when the temperature increases, the C_5–C_6 introduction toward the aromatization steps would be favored. The aromatic hydrocarbons were the main products obtained at both temperatures studied, reaching values of 10 and 45% at C_1 molar fraction of 0.4, GHSV(LPG) = 810 ml/g h and 450 and 550 °C, respectively. These are the final products of an overall process of aromatization, where a large number of reactions occurs simultaneously. The methane and LPG (propane, butane and isobutane) transformation involves a network of complex reactions such as dehydrogenation, cracking, hydrocracking or hydrogenolysis, dimerization and/or oligomerization, dehydrocyclization (or aromatization) and dealkylation (or demethylation).

4. Conclusions

The catalytic transformation of LPG (C_3, C_4 and i-C_4) is improved by decreasing the GHSV(LPG). The i-C_4 conversion, the more reactive LPG component, approaches 98% at GHSV(LPG) = 810 ml/g h, at 550 °C, over Zn-ZSM-11 and using only LPG as the feed.

When a gas mixture LPG + C_1 is used as the feed, LPG is able to activate methane even at very high C_1 molar fractions in the feed ($C_1/(C_1 + \mathrm{LPG}) = 0.85$). The temperature increase as well as the decrease of GHSV(LPG) and C_1 molar fraction in the feed favor the C_1 and LPG transformation. The C_1 activation could occur through its interaction with the more reactive LPG component, i-C_4. The C_1 and i-C_4 conversion remains almost constant at C_1 molar fractions lower than 0.6, reaching 10 and 96%, respectively, at GHSV(LPG) = 810 ml/g h, at 550 °C, over Zn-ZSM-11. The aromatic hydrocarbons are the main reaction products, rising to excellent levels (45%) at C_1 molar fraction 0.4, GHSV(LPG) = 810 ml/g h and at 550 °C, over Zn-ZSM-11. These products arise from the aromatization of C_1, C_3, C_4 and i-C_4 hydrocarbons (present in the feed) occurring simultaneously over the Zn-ZSM-11 catalyst.

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