Catalytic activation of methane using *n*-pentane as co-reactant over Zn/H-ZSM-11 zeolite

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The catalytic conversion of methane (C1) into higher hydrocarbons using *n*-pentane (*n*-C5) as co-reactant over Zn/H-ZSM-11 zeolite material was studied. The aromatics yield was very high, achieving values of over 40 mol% at 500 °C and $w/f = 30\,\mathrm{g\,h\,mol^{-1}}$ with a C1/(C1 + C5) molar fraction (XC1) = 0.30. Contact time and time-on-stream effects on the product distribution were analyzed in detail in order to obtain information about the evolution of different species. The C1 conversion was as high as 30 mol% without CO_x reaction products.

KEY WORDS: methane conversion; co-reactant; *n*-pentane; higher hydrocarbons; Zn zeolites.

1. Introduction

Chemical utilization of short-chain alkanes (less than 6 carbon atoms) is one of the dominant scientific challenges in the field of petrochemistry. These compounds are present in natural gasoline (constituted by ethane (C_2) = 2.4, butane (C_4) = 1.3, pentane (C_5) = 67.1, hexane (C_6) = 22.0, heptane (C_7) = 5.7, and octane (C8) = 1.5% w/w) [1], liquefied petroleum gas (LPG) (C3 = 38.7, iC4 = 36.3, and C4 = 25.0 mol%) [2], and natural gas (constituted by methane (C1) = 82.8, C2 = 16.1, and C3–C4 = 1.1% w/w) [3]. Furthermore, refinery processes such as fluid catalytic cracking (FCC) and hydrotreating operations produce large amounts of saturated compounds. Thus, our target is the direct transformation of lower alkanes for application as aromatics, for instance in blending to enhance the octane number of gasoline (despite strong environmental restrictions for the legal content of benzene in gasoline [4]), to produce more valuable raw chemical products in the petrochemistry industry, and to get liquids transportable by existing petroleum pipelines, especially for remote regions.

ZSM-5 and ZSM-11 zeolites have been extensively studied as catalysts for aromatization of light paraffins [5–7]. Modified ZSM zeolite materials with Zn or Ga have been successfully used for this purpose [8], and Inui [9] described the effect of these in paraffin conversion. Anunziata *et al.* have reported that Zn-ZSM-11 shows excellent aromatization behavior for ethane (C2), propane (C3), LPG, and light gasoline (*n*-C5, *n*-C6, *n*-C7) [10–12]. Methane (C1), the main component of natural gas (up to 90% w/w depending on the source [13]), is the lowest paraffin and the hardest to activate because of its high stability–low reactivity. Wang *et al.* [14] and Pierella *et al.* [15] reported C1 aromatization in the presence of small amounts of light hydrocarbons under non-oxidizing conditions on transition metal ions supported on H-zeolite. In previous papers, aromatization of C1 using different light paraffins as co-reactants was reported using Zn-ZSM-11 catalyst [2,3,15,16]. Now, we progress to the functionalization of C1 using *n*-C5 as a co-reactant. Thus, this work deals with the activation of C1 with *n*-pentane, the main product present in natural gasoline.

2. Experimental

Catalytic reactions were carried out in a fixed-bed continuous flow quartz reactor, with a 10 mm diameter, at 1 atm total pressure. This reactor was operated on-line with a gas chromatograph equipped with FID-TC detectors. Products were withdrawn periodically from reactor outlet, and analyzed using a 2.2 m Porapak column. The delivery tubes were all heated to 250 °C at the exit of the reactor to avoid liquid condensation in the pipework. Feedstocks used in this study were high-purity methane (>99.97% w/w) supplied by AGA and *n*-pentane (99.5% w/w) supplied by Ciccarelli. The reactions were carried out first using N_2 + *n*-C5 as feed at different molar fractions of N_2, with the objective to study the effect of the partial pressure of *n*-C5 on its conversion in the presence of an inert gas. Then, methane was used instead of N_2 under the following reaction conditions: methane XC1 (= C1/(C1 + *n*-C5)) from

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0.27 to 0.74, at a constant temperature of 500 °C, a contact time $w/f(n\text{-C5}) = 7.2\,\text{g h mol}^{-1}$, and time on stream (TOS) = 20 min. To analyze intermediate species we used a constant C1 molar fraction of 0.3, temperature of 500 °C, $w/f(n\text{-C5}) = 1.5\text{–}30\,\text{g h mol}^{-1}$, and a TOS between 20 and 275 min. Conversion, selectivity, and reaction product yields were expressed on a molar carbon atom basis. The Zn/H-ZSM-11 catalysts (Si/Al = 17), with different zinc molar fraction ($ZN^{2+}/ZN^{2+} + H^{+}$) [17,18], were synthesized and characterized by XRD, BET, FTIR, EDX, ICPE, and XPS.

Table 1
Catalytic activity of H-ZSM-11 and various Zn-containing zeolites

Catalyst	Cation (mol/cell unit)[a]		C1 conversion	*n*-C5 conversion
	Al	Zn		
H-ZSM-11	5.20	–	1	64.3
Zn/H-ZSM-11 (a)	5.30	0.54	5.4	59.1
Zn/H-ZSM-11 (b)	5.33	1.33	16.2	54.5
Zn/H-ZSM-11 (c)	5.38	2.13	32.9	51.7

Note: Temperature = 500 °C; $X\text{C1} = 0.3$; n-C5 $w/f = 15\,\text{g h mol}^{-1}$.
[a] ICPE.

3. Results and discussion

Preliminary catalyst-screening tests revealed that the best results for C1 conversion were obtained with Zn/H-ZSM-11 (c) catalyst. H-ZSM-11 is active for *n*-C5 conversion but the C1 conversion is very poor. The C1 conversion increases with the Zn content. Thus the activation of C1 with *n*-C5 was studied using sample (c). The results are shown in table 1.

According to EDX and XPS characterization results for H-ZSM-11 and sample (c), the zinc was incorporated only slightly in the outer surface region of the zeolite crystallites. In the same way, the results obtained from XRD patterns and BET indicated a high purity of the samples (see table 2).

Infrared analysis of the samples was carried out using a JASCO 5300 FTIR spectrometer on self-supported wafers. The studies were performed using the wafers in a temperature-controlled cell with CaF_2 windows connected to a vacuum line, and evacuated at 10^{-4} torr for 4 h at different temperatures, to determine the strength and nature of the active sites using pyridine as a probe molecule. Results represented by the amount of pyridine ($\mu\text{mol g}^{-1}$) retained after desorption (under the conditions described above) are reported in table 3. As can be seen, sample (c) possesses a higher amount of SLS than H-ZSM-11 sample, with very few strong Brønsted centers.

3.1. $N_2 + n\text{-C5}$ studies

Reference studies performed for *n*-C5 conversion and yields employing different molar fractions of $N_2/(N_2 + n\text{-C5})$ and n-C5 $w/f = 30\,\text{g h mol}^{-1}$ (see table 4) showed that, with increasing partial pressure of N_2, *n*-C5 conversion decreases sharply and the conversion falls to near 0% at $XN_2 \approx 0.96$. The C1 formation in the range under study ($XN_2 = 0.03\text{–}0.84$) reached a maximum yield of about 1.61 mol% at a XN_2 value of 0.36; propane, butane, and ethane yields reached about 2–4 mol%.

Maximum *n*-C5 conversion was obtained at $XN_2 = 0.03$ where the C1 yield was 1.6 mol%. These results suggest that *n*-C5 cracking does not favor high C1 yields, see table 4, and the terminal cracking activity (C_1sp^3–Hs bond of the *n*-C5) is lower than the cracking of C_2sp^3–C_3sp^3 [19]. In the same way, considering the high proportion of aromatic hydrocarbons (AH), hydride abstraction without cracking appears to be the main pathway of the reaction under study. The SLS present in the catalyst (see table 3) suggests that the high concentrations of hydrogen acceptor and dehydrogenation sites lead to high levels of *n*-C5 conversion and AH yields.

3.2. C1 + *n*-C5 studies

3.2.1. *Effect of partial pressure*

The influence of the feed molar fraction C1/(C1 + *n*-C5) (XC1) was studied from 0.38 to 0.75 at $w/f(n\text{-C5}) = 7.2$, 500 °C, and 1 atm total pressure. The conversions of C1 and *n*-C5 are plotted in figure 1. The C1 conversion is approximately 27 mol% at the lower value of XC1 studied. Taking into account our previous report (using C1 + LPG as feed [15], where, for C1 molar

Table 2
Chemical composition, mean crystal size, external surface of the crystallites, and crystallinity of H-ZSM-11 and Zn/H-ZSM-11 (c)

Catalyst	Chemical composition						Surface area, BET ($m^2\,g^{-1}$)	Crystal size, SEM (μm)	Crystallinity, XRD (%)
	(Si/Al)			Al/Zn					
	ICPE	EDX	XPS	ICPE	EDX	XPS			
Na-ZSM-11	17.2	18.5	61	–	–	–	412	1.3 × 1.2 × 3.5	>99.0
Zn/H-ZSM-11	16.9	18.0	62	4.0	3.45	97	398	1.2 × 1.2 × 3.45	>98.5

Table 3
FTIR results[a] according to the amount of pyridine retained after desorption at different temperatures (10^{-4} torr, 4 h)

Catalyst	Amount of pyridine (μmol g^{-1})					
	WBS	MBS	SBS	WLS	MLS	SLS
H-ZSM-11	74	90	81	0.7	0.03	0.01
Zn/H-ZSM-11 (c)	2.4	5.2	2.3	12.6	10.8	22.4

[a] Pyridine retained at 350–250 °C (WBS, weak Brønsted sites; WLS, weak Lewis sites); at 400–350 °C (MBS, medium Brønsted sites; MLS, medium Lewis sites); at 400 °C (SBS, strong Brønsted sites; SLS, strong Lewis sites).

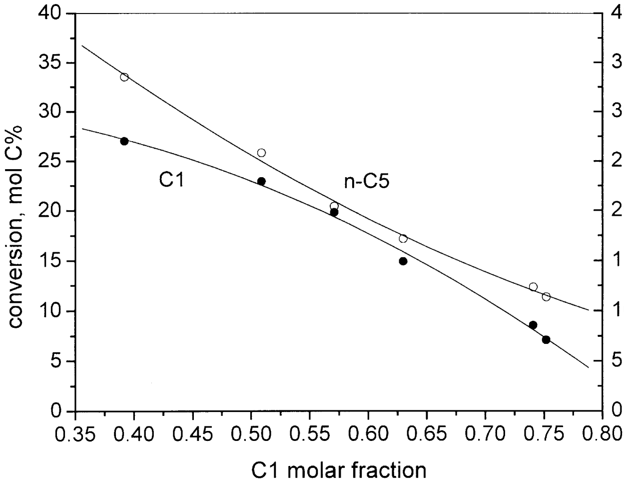

Figure 1. C1 and n-C5 conversion *versus* C1 molar fraction in the feed. Temperature, 500 °C; pressure, 1 atm; contact time, 7.2 g h mol^{-1}; over Zn/H-ZSM-11 (c).

fraction of 0.4, the C1 conversion at 550 °C and w/f(LPG) = 5.48 g h mol^{-1} over Zn-H-ZSM-11 was almost 10 mol%), it appears that the use of n-C5 as an additive to the C1 feedstock is about three times more effective in promoting C1 conversion. At the highest XC1 evaluated (C1/(C1 + n-C5) = 0.82), the C1 conversion was similar, approximately 5 mol% in both cases.

Figures 2 and 3 show the product distributions as a function of XC1, at w/f(n-C5) = 7.2, 500 °C, and 1 atm total pressure, for light hydrocarbons and individual AH, respectively. At low XC1 the main products are AH and C3 (propane) and C3= (propylene); their production decreases as XC1 increases. Toluene and xylenes are the principal AH obtained from the interaction of C1 and n-C5 at different XC1 (figure 3). Thus, the increasing yields of higher hydrocarbon reaction products (AH) as XC1 decreases mostly parallel conversion (figure 1).

3.2.2. *Effect of contact time*

The activation of C1 with n-C5 as co-reactant (over sample (c)) using a C1 molar fraction XC1 = 0.3, at 500 °C, total pressure 1 atm, and different contact times, was also studied. The C1 and n-C5 conversion and AH yield plotted as a function of w/f are shown in figure 4. It can be seen that in the whole range of contact time evaluated, the aromatization reactions are in a non-equilibrium state and the active sites on the catalyst remain active. The n-C5 and C1 conversions increase as w/f increases, but C1 conversion approaches a limit of about 40 mol%. It appears that the distribution of reaction intermediates and their products selectivity change at long contact time. According to the data of table 4 and figure 4, it appears that one of the primary roles of methane is to increase pentane conversion. Comparing the conversion of n-C5 in the presence of N_2 at 30 g h mol^{-1} (table 4) and in the presence of C1 (figure 4), at the same C1 molar fraction and the same w/f value of 30, n-C5 conversion reaches 52.7 and 80%, respectively.

Table 4
Conversion and product distribution for $N_2 + n$-C5 as feed over Zn/H-ZSM-11 at different partial pressures

	$N_2/(N_2 + n$-C5)			
N_2 partial pressure	0.03	0.36	0.75	0.84
n-C5 conversion	59.5	52.7	34.7	18.2
Product distribution (mol% C)				
C1	1.2	1.6	0.9	0.4
C2=	2.5	3.5	3.8	3.0
C2	4.2	5.3	2.4	1.1
C3	9.4	11.0	8.4	5.6
C4	5.3	6.6	4.7	2.4
AH	36.9	24.7	14.4	5.9
C5	40.5	47.3	65.3	81.8

Note: Temperature = 500 °C, n-C5 w/f = 30 g h mol^{-1}, TOS = 20 min, total pressure = 1 atm.

3.2.3. *Effect of time on stream*

We also studied the influence of time of reaction on the feedstock conversion and aromatic and light

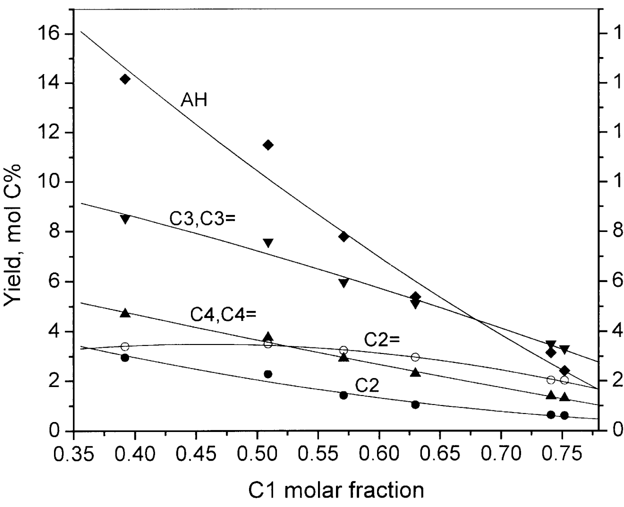

Figure 2. Light hydrocarbons *versus* C1 molar fraction in the feed. Temperature, 500 °C; pressure, 1 atm; contact time, 7.2 g h mol^{-1}; over Zn/H-ZSM-11 (c).

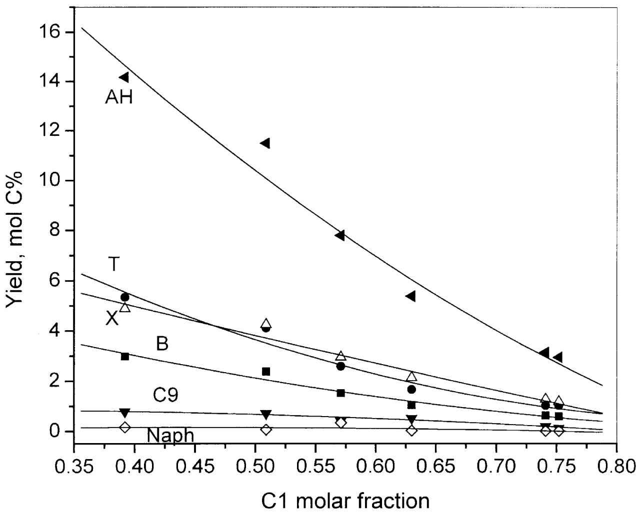

Figure 3. Distribution of aromatic hydrocarbons *versus* C1 molar fraction in the feed. Temperature, 500 °C; pressure, 1 atm; contact time, 7.2 g h mol^{-1}; over Zn/H-ZSM-11 (c).

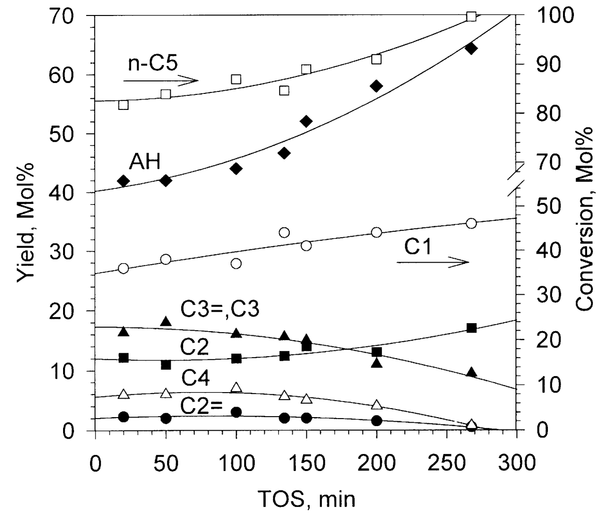

Figure 5. TOS influence on the C1 and *n*-C5 conversion and yield of AH and light paraffins. *w*/*f* = 30; over Zn/H-ZSM-11 (c); temperature, 500 °C; feed XC1 = 0.3.

hydrocarbon yield at 500 °C, molar fraction C1/(C1 + C5) = 0.3 at 30 g h mol^{-1}. The results are shown in figure 5. It can be seen that C1 conversion increases somewhat during the reaction time studied, between 0 and 275 min, whereas *n*-C5 with time reaches total conversion under these conditions. Total aromatics and ethane yields and selectivities increase with time to as much as 60 and 20 mol%, respectively. Thus, Zn/H-ZSM-11 (c) catalyst is not deactivated by coke deposition and the active sites of the catalyst are capable of aromatizing the feedstock under these conditions. The yields of C2= and C2+ hydrocarbons decrease with increasing reaction time reflecting possible changes in the distribution of active sites or intermediates. The effective C1 conversion indicates that direct activation of methane was achieved.

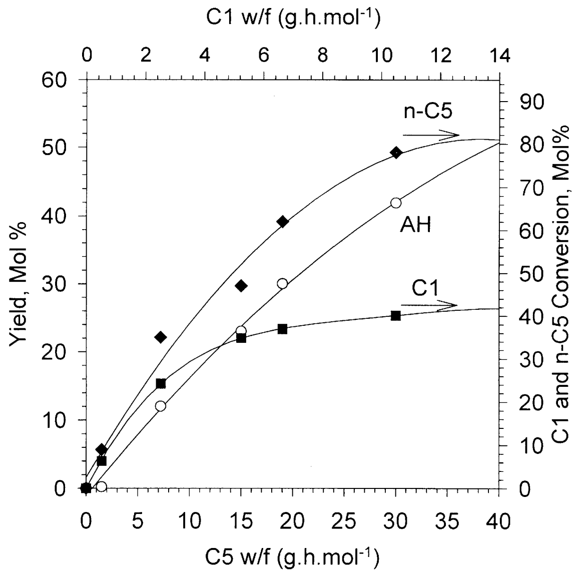

Figure 4. C1 and *n*-C5 conversion and aromatic hydrocarbons (AH) yield *versus* *n*-C5 and C1 contact time. C1 molar fraction (C1/(C1 + *n*-C5)) = 0.3; temperature, 500 °C; pressure, 1 atm; TOS = 0; over Zn/H-ZSM-11 (c).

3.2.4. *Application of optimum performance envelope technique*

Figure 6 shows the light hydrocarbons yield *versus* *n*-C5 and C1 conversion, with XC1 = 0.3 at 30 g h mol^{-1}, 500 °C, and TOS = 0, according to the standard optimum performance envelope (OPE) technique [20,21]. Ethylene begins to be formed even at low conversion levels (for C1 and *n*-C5 conversion), and its yield goes through a maximum and decreases with further increase of the total conversion, indicating a secondary transformation. A similar effect on the conversion was detected

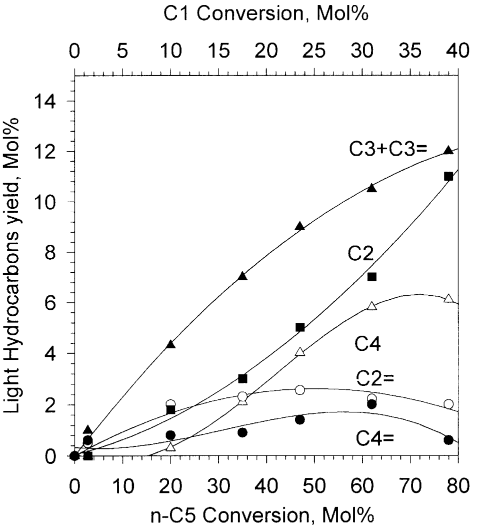

Figure 6. Light hydrocarbons yield as a function of C1 and *n*-C5 conversion according to the OPE technique. XC1 = 0.3; temperature = 500 °C; total pressure = 1 atm; TOS = 0; over Zn/H-ZSM-11 (c).

for most C3 and C4 products. C4 appeared as a secondary and unstable reaction product, whereas C2 is a stable secondary reaction product. Aromatics yield (not shown in figure 6, but taking account of the data shown in figure 4 (even at $TOS = 20\,min$)) appears only at higher conversion levels and increases as *n*-C5 conversion increases. Thus aromatic hydrocarbons are stable secondary reaction products.

Moreover, analyzing the evolution of aromatic hydrocarbons, we can see that they are secondary and stable reaction products. As reported in table 3 [3,17], metal species incorporated on the zeolite framework as a counter ion increase the number of strong Lewis sites (SLS) and would produce high concentrations of hydrogen acceptor species. Thus, dehydrogenation would be favorable leading to higher levels of conversion and AH yields. The presence of acid Brønsted sites would promote the cracking activity through protonation of reactive species and formation of carbonium species. The function of Zn loaded in the zeolite appears to be the dehydrogenation of *n*-C5 and cracking products (C2, C3, C4) into their corresponding olefins (C2=, C3=, C4=) and carbenium species formed from them, and conversion of the naphthenic intermediates into aromatics. The first step would be the adsorption of *n*-C5 species on the surface of the catalyst and abstraction of a hydride producing a carbenium-like ion through EDA (electron donor–acceptor) active sites, which would allow C1 activation by interaction with adsorbed species. Then, reactive species (olefins and carbenium intermediates) undergo secondary transformations. The presence of strong Lewis sites (SLS) on the catalyst prevents hydrogenation of intermediate alkenes, which would be efficiently introduced into polymerization, cyclization, dehydrogenation, and aromatization complex mechanisms. In this way, the cracking steps of oligomer species and subsequent polymerization explain the distribution of aromatic products.

4. Conclusion

Methane was efficiently converted into higher hydrocarbons under non-oxidation conditions over Zn/H-ZSM-11. The Zn-containing H-ZSM-11 catalyst acts as a hydride acceptor generating C2=, C3=, C4=, and their carbenium species (highly reactive intermediates) on SLS, through an EDA adduct, which enables C1 activation with high productivity. Aromatics appear as the main products reaching yields as high as 42 mol% at 500 °C and $30\,g\,h\,mol^{-1}$. Thus, the *n*-C5 would be an appropriate co-reactant for C1 conversion to aromatics. Moreover, the use of natural gasoline, with low commercial value, is an interesting feed to be used as co-reactant in C1 activation.

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