Methane transformation using light gasoline as co-reactant over Zn/H-ZSM11

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The catalytic conversion of methane (C1) to aromatic hydrocarbons (AH) such as benzene, toluene and xylenes (BTX) over a Zn/H-ZSM-11 catalyst using Light Gasoline (C5 + C6) as co-reactant was studied. AH yields were as high as 30 %mol at 500 °C, w/f = 40 g h mol^{-1} at C1 molar fraction = 0.20. The 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 reached 36 mol% C using Zn/HZSM-11 with content of 2.13 mol of Zn^{2+} per cell unit.

KEY WORDS: Zn/HZSM-11; methane activation; light gasoline; co-reactant.

1. Introduction

The dependence on oil last century is expected to be gradually offset in this century by increasing dependence on natural gas. Thus, it has been of considerable interest to convert natural gas into more commercially useful chemicals and liquid fuels. On the other hand, natural gas is currently being used for home and industrial heating as well as for the generation of electrical power. Moreover, the reserves are increasing more rapidly than those of liquid petroleum, and it is anticipated that this trend will extend into the 21st century. Methane (C1) is the principal component of most natural gas world reserves [1], consequently, its direct conversion is under extensive study but despite the enormous experimental efforts done, many aspects of that remain as challenging scientific and catalytic topics of ongoing discussion.

The use of metal-exchanged zeolites, particularly exchanged Ga and Zn/H-zeolites, ZSM-5 and ZSM-11 [2–5] to catalyze dehydro-cyclo-dimerization reactions improves the selective conversion of light alkanes (C1–C4) to aromatics via non-oxidative routes. In 1993, Wang *et al.* [6] reported on the dehydro-aromatization of C1 under non-oxidizing conditions on H-ZSM5 catalyst modified with Mo and Zn, and denoted that benzene yield increases with the increasing of the C1 partial pressure. Previously, they [7] informed that adding an alkene in the feed as co-reactant, it plays a role of initiating species. Solymosi and Szöke [8] reported high ethane (C2) conversion and benzene selectivity using

MoC/ZSM-5 at 700 °C. Considering this conclusions and taking account of the chemical similarity between ethane and methane Pierella *et al.* [9] studied C1 transformation over Mo-HZSM11 at lower temperature (500–600 °C). They used a mixture of C1 and C2$^+$ as feed, obtaining a C1 conversion of 27% and a BTX (benzene, toluene and xylenes) yield of 32.7 mol C %. Moreover, very high levels of C1 to aromatic hydrocarbons with C1 + C2 as feed at 550 °C, 1 atm, over Zn-HZSM11, and 40% of AH yield was reported [10]. Liquefied petroleum gas (LPG) also was studied as co-reactant with C1 [11]; C1 conversion up to 6%mol and selectivity to higher aromatics as high as 82.5% mol at 550 °C over Zn-exchanged H-ZSM11 (Zn^{2+}/(Zn^{2+} + H$^+$) = 0.86) were obtained. Furthermore, the addition of co-reactants is a useful tool to overcome the thermodynamic limitation of a direct conversion [12].

Light gasoline (LG), a rich pentanes and hexanes refinery cut (with little amounts of ethane, propane, butane and heptanes), is very low valued as industrial feedstock. Anunziata and Pierella [13] studied Light Gasoline over ZSM-5, ZSM-11 and SABO-11 Zn-exchanged catalysts, at 500 °–540 °C in order to obtain higher hydrocarbons on the range of the aromatics (BTX). The Light Gasoline conversion reached at 100% with high selectivity to BTX, up to 60.2%.

Beside, recently experiments published by us [14,15], on the direct catalytic dehydrogenation and aromatization of C1 to AH in absence of oxidizing conditions were carried out with a feedstock, formed by C1 + C5 and C1 + C6. In the same work, C1 appears, in a little quantity and as secondary reaction product when we

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used N2 + C5 or N2 + C6 only. Although C1 appears during the aromatic formation and grows constantly along the reaction with the contact time of the reactant, its yield was less than 3 mol%, so is regarded as neglect. In this work, those results allowed us to choose the best conditions to improve C1 conversion using LG as co-reactant over Zn/H-ZSM11. Thus, the object of this work is to achieve the highest levels of methane conversion using light gasoline as co-reactant taking advantage to the this gasoline cut, that nowadays has a lower commercial value because it is only used as a poorer quality solvent.

2. Experimental

The catalysts preparation and the catalytic system employed in the methane (C1) + Light Gasoline (LG) conversion were described elsewhere [14]. The catalysts characterization was determined using BET, XRD, SEM, ICPE, EDX and XPS. The results obtained are shown in table 1. The samples used in this work are denoted as: Zn/HZSM-11 (a), Zn/HZSM-11 (b), Zn/HZSM-11(c) with 0.54, 1.33 and 2.13 mol of Zn^{2+}/cell unit, respectively (table 2).

Catalytic reactions were carried out in a fixed-bed continuous flow quartz reactor with a 10 mm inner diameter; the reactor was designed to minimize homogeneous reactions. The reactor was operated at atmospheric pressure. Products were withdrawn periodically from the outlet of the reactor. Liquid products of the reaction were accumulated in a cooler-tramp, at a constant temperature of −15 °C. Gaseous products as well as non-condensed heavier products were cooler-separator and were collected to a wet-gas tramp. Gaseous and liquid products were analyzed with a GC equipped whit a FID/TCD and a 2.2 m Poparak Q column. Feedstock used in this study were: high-purity methane (> 99.97%w/w) supplied by AGA and light gasoline supplied by (YPF): The light gasoline (LG) composition (wt%) was mainly n-pentane and n-hexane (67.1 and 23% w/w respectively). Methane molar fractions XC1: C1/(C1 + LG) ranging from 0.2 to 0.7 were varied at 500 °C. The contact time W/F (LG) was varied from 1 to 40 g h mol^{-1} and the time on stream (TOS) from 20 to 250 min, under non-deactivating conditions. In order to perform the partial pressure studies of C1 a W/F (LG) of 40 g h mol^{-1} was chosen.

The mass balance for each experimental result was calculated from a combination of the gas-chromatographic data, the weight of the collected liquid products, and the amount of resulting gases. Conversion and yield of the products were expressed on molar carbon atom basis.

Pyridine adsorbed on the samples followed by FTIR, was carried out using a JASCO 5300 FTIR spectrometer on self-supported wafers (10 mg). The studies were performed using temperature-controlled cell with a CaF_2 window connected to a vacuum line, the wafers were evacuated at 10^{-4} torr for 4 h at 250, 350 and 400 °C, to determine the strength and nature of the active sites using pyridine as a probe molecule. Infrared spectra of pyridine adsorbed on acidic catalysts showed absorption bands at 1450 and 1550 cm^{-1} indicating the presence of both, Lewis and Bronsted acid sites. The concentration of PyH$^+$ (pyridine interacting with Bronsted acidic sites) was calculated from the maximum intensity of the absorption peak at 1545 cm^{-1}. We calculated the concentration of the Lewis-acid sites using the intensity of the bands at 1450–1460 cm^{-1}. This absorption indicates the formation of the electron-donor-acceptor adduct EDA, of pyridine-Lewis sites in the zeolite. The amount of Brönsted and Lewis sites was determined using literature data on the integrated molar extinction coefficients [16].

3. Results and discussion

3.1. Catalyst characterization

According to the ICPE, EDX and XPS characterization results of H-ZSM-11 and Zn/H-ZSM-11 samples (a, b and c), the zinc was incorporated slightly on the outer surface of the zeolite crystals. In the same way, the results obtained by XRD patterns and BET indicated a high purity of the samples (see table 1).

Table 1
Catalysts characterization by: ICP, EDX, XPS, BET, SEM and crystallinity by XRD

Catalyst	Chemical Composition						Area, BET (m^2/g)	Crystal size SEM (μm)	Cryst. XRD (%)
	Si/Al[a]			Al/Zn[a]					
	ICPE	EDX	XPS	ICPE	EDX	XPS			
Na-ZSM-11	17.2	18.5	93.0	–	–	–	412	1.3×1.2×.3.5	100
Zn/H-ZSM-11(a)	17.0	18.2	93.5	16.0	16.2	98.7	405	1.25×1.2×3.5	> 99.5
Zn/H-ZSM-11(b)	17.0	18.2	93.5	6.6	6.8	97.0	400	1.23×1.2×3.5	> 99.0
Zn/H-ZSM-11(c)	16.9	18.0	94.0	5.0	5.4	93.0	398	1.2×1.2×3.4	> 98.5

[a] Molar ratio.

Table 2
C1 conversion and FTIR data of acid sites for H-ZSM11 zeolite and Zn/H-ZSM-11 samples, using pyridine as a probe molecule at different desorption temperature and 10^{-4} Torr

Catalyst[a]	C1 + LG		FTIR[c] Py (μmol/g)					
	C1 Conv. [b]	LG Conv. [b]	350–200 °C		400–350 °C		>400°C	
			WBS	WLS	MBS	MLS	SBS	SLS
H-ZSM-11	0.5	59,3	93	7	79	5	74	3
Zn/H-ZSM-11 (a)	3.0	63,0	47	76	71	56	49	127
Zn/H-ZSM-11 (b)	12.7	76,4	41	95	65	74	41	158
Zn/H-ZSM-11 (c)	23.2	89,8	24	146	51	108	22	243

[a] Mol Zn^{2+}/cell unit = 0.54, 1.33 y 2.13, for samples a, b and c, respectively.
[b] Mol% C. Reaction conditions: w/f (C1) = 15 g h mol^{-1} and w/f (LG) = 98 g h mol^{-1}. Feed: C1 + LG, molar fraction C1: XC1 = 0.50; TOS = 20 min; 500 °C; total pressure: 1 atm.
[c] Pyridine retained at different temperatures and 10^{-4} Torr during 4 h. BS: Brönsted sites; LS: Lewis sites. W: weak, M: medium and S: strong.

3.2. Catalytic activity: Preliminary studies

Preliminary tests over Zn-ZSM-11 catalysts with different amounts of Zn^{2+} were carried out to asses the catalyst performance for the activation of methane using light gasoline as co-reactant to produce higher hydrocarbons with the least amount of side products. The results obtained for C1 and LG conversion from C1 + LG feedstock using an arbitrary fraction molar of C1 (C1/(C1 + LG)) = 0.50, at 500 °C and atmospheric pressure, are shown in table 2.

In order to determine the strength and nature of the active sites, studies of FTIR were performed using pyridine as probe molecule. Taking account the FTIR results and the C1 conversion from each sample (table 2), methane activation is strongly influenced by the nature and concentration of the active sites on the catalysts. Thus, by the introduction of Zn^{2+} as counter ion, we generate new and strong Lewis acid sites. Moreover, the amount of pyridine retained from different type acid sites of the catalysts, after desorption (under the conditions described in experimental section) are also shown in table 2. According to these data is evident that the C1 conversion increases as the zinc content increases.

Considering the best performance of sample (c), we choose this sample in the further studies, to determine the influence of different reaction parameter, table 2.

3.3. Light gasoline conversion

A set of reactions were performed in order to determinate the conversion of light gasoline and total aromatic yields. The experimental conditions were: temperatures 500 and 540 °C, time on stream 60–90 min and atmospheric pressure, see table 3.

The reaction products were alkanes (C1, C2, C3, C4), alkenes (C2 =, C3 =, C4 =), iso-alkanes (manly iC4) and aromatic hydrocarbons, composed by: benzene, toluene, xylenes, trimethylbenzenes and other C9+ hydrocarbons. Non condensed polyaromatic hydrocarbons were found in the conditions studied, see table 4.

Zn species into H-ZSM11 improve the LG conversion and aromatic hydrocarbons yield and inhibit cracking side reactions, in agreement with Biscardi and Iglesia [17] and Inui [18] results. Zn catalyzed the initial transformation of lineal alkanes, pentanes and hexanes, into intermediate ions and allowed their introduction into the complex aromatization mechanism. We can see that at the lowest temperature studied, the catalyst showed a higher AH yield than at higher temperature.

3.4. C1 + light gasoline conversion.

3.4.1. The effect of partial pressure

The effect of methane (C1) partial pressure in light gasoline (LG) at the constant contact time W/F of 40 g h mol^{-1}, 500 °C and 1 atm. of total pressure were studied. When methane molar fraction was equal to 0, the LG reached 95 mol% of conversion, and the reaction products distribution were detailed in table 4.

In the same way, figure 1 shows C1 and light gasoline conversion at different molar fraction of C1 from 0.0 to 0.6, at 500 °C. According to the data shown in this figure, C1 and LG conversion increased as the C1 molar fraction decreased. At medium C1 molar fraction (or partial pressure) its conversion reaches 51.10 mol%, with the increasing of its molar fraction, the light gasoline conversion is not affected by the increasing C1 molar fraction in the feed.

It can be seen, that AH are the main reaction products at lower C1 partial pressure reaching as high as 25 mol%. The higher light gasoline conversion at the lower C1 molar fraction indicates, that their compounds are the first to achieve the active sites to be transformed into intermediates species. Over this intermediates the C1 molecules from the gas phase would impact allowing its incorporation into the complex mechanism of aromatization.

The results allowed us to suggest that the reaction mechanism would be a Rideal–Eley one, where C1 impact from the gas phase over formed species by the C5 and C6 adsorption on the catalyst active sites (Zn^{2+} species).

Table 3
Light gasoline and aromatic hydrocarbons yield using H-ZSM11 zeolite and Zn/H-ZSM-11(c)

Catalyst	Chemical composition (XRF)		LG Conversion[a]		AH[b] Yield[a]	
	Si/Al	Al/Zn	Temperature (°C)		Temperature (°C)	
			500°C	540°C	500°C	540°C
H-ZSM-11	18.12	–	96.00	100.00	22.0	20.0
Zn/H-ZSM-11(c)	20.77	6.0	95.00	100.00	35.00	30.04

[a]Mol% C. Feed: Light gasoline. Reaction conditions: w/f (LG) = 70 g h mol^{-1}; TOS: 60 min; total pressure 1 atm.
[b]Total aromatic hydrocarbons.

Table 4
Conversion and product distribution for light gasoline (LG) as feed over Zn/HZSM-11(c) at different temperatures [a]

Temperature (°C)	500	540
LG Conversion (Mol% C)	95.0	100.0
Product Distribution (Mol% C)		
Methane	5.48	13.25
Ethane	11.45	18.54
Propane	39.03	35.02
Butanes	4.03	3.15
Benzene	6.87	5.52
Toluene	13.19	12.47
Xylenes	9.14	7.21
Trimethylbenzenes,	5.75	4.33
Total Aromatic hydrocarbons	35.01	30.04

[a]Reaction conditions: Feed: Light Gasoline LG; w/f
(LG) = 70 g h mol^{-1}; TOS: 60 min; total pressure 1 atm.

Carbenium-type ions are generated by the hydride abstraction over the acceptor electron sites (Lewis acid sites) of the Zn/H-ZSM-11catalyst sample (c).
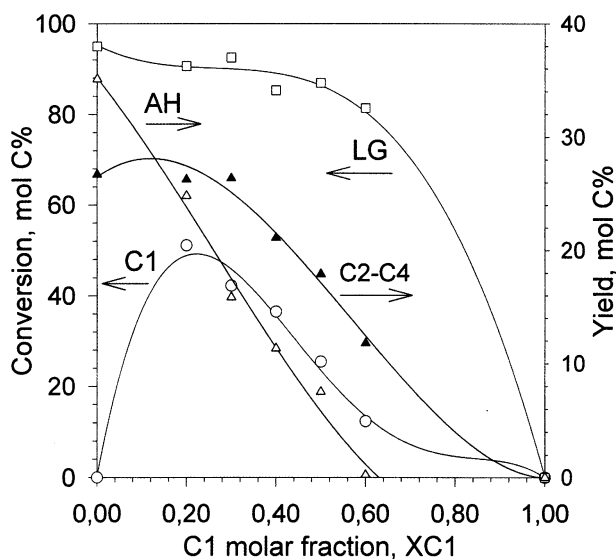

Figure 1. Light gasoline (LG) and methane (C1) conversion vs. methane molar fraction in the feed. Temperature: 500 °C. Total pressure: 1 atm. Contact time w/f (NG): 40g h mol^{-1} using Zn/H-ZSM-11(c) catalyst.

3.4.2. Effect of the C1 contact time

Methane activation using light gasoline as co-reactant, over the Zn/H-ZSM11(c) catalyst was studied with a feed of C1 molar fraction, XC1 (C1/(C1 + LG)) = 0.50, at 500 °C, atmospheric pressure and different contact time extrapolated at TOS = 0. In figure 2 is shown that C1, C5 and C6 conversion grew along the contact time. However, the C5 conversion would reach the equilibrium before the other reactants.

The rate of C5 conversion would be initially higher because of its partial pressure in the feed mixture, thus this would be the first species to reach the catalyst active sites and then it would be the responsible to active firstly the C1 molecule. As the contact time increases the equilibrium between the ionic species from pentanes and hexanes.

Nevertheless, hexyl-carbenium would be more stable over the catalyst sites than pentyl-carbenium ones. C1 from the gas phase would impact indistinctly over these different ionic species.

However, methane conversion achieved faster the equilibrium than hexanes (C6) in the contact time range studied. It would be another evidence of the mechanism that govern these reactions, which lead to the C1 activation, more precisely funtionalization.

The main products were the aromatic ones while the alkanes and alkenes between 2 and 4 atoms of C were less than 10 mol% C. That passes through a maximum showing the effectiveness of the aromatization steps over the cracking ones.

The exchanged zeolite support acid-catalyzed oligomerization and cyclization reactions would convert these light hydrocarbons into higher hydrocarbons as aromatics. Therefore, the load of Zn^{2+} as counter ion over the catalyst surface generates the active Lewis acid sites for the adsorption of co-reactant molecules by the hydride abstraction. It become into a very reactive intermediates as alkenes and naphthenic-type. C1 impact from gas phase onto these adsorbed species to be activated.

As C1 partial pressure is medium (XC1 = 0.50) the active site coverage is medium too, generating ad-species C5+ type. The C1 can react with these intermediates with high efficiency. However, when only few active sites
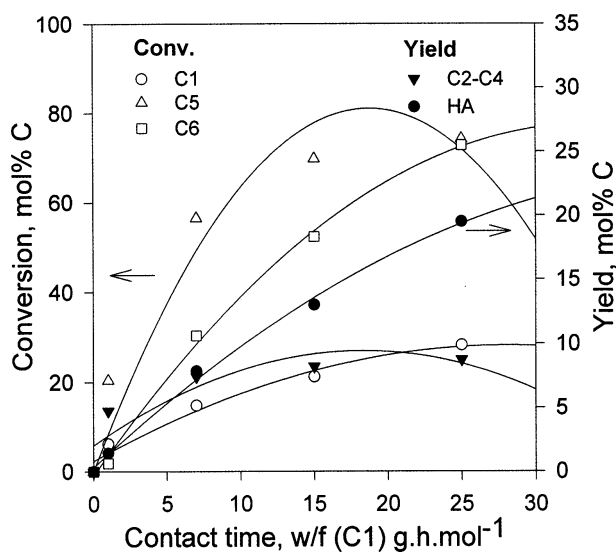
Figure 2. C5, C6, C1 conversion and C2–C4 light hydrocarbons and aromatic hydrocarbons vs. C1 contact time. Temperature: 500 °C. Total pressure: 1 atm. Feed: C1 fraction molar: XC1 = 0.50; TOS = 0, on Zn/H-ZSM-11(c) catalyst.

Figure 3. OPE plot. C2–C4 and aromatic hydrocarbons yield vs. C1 conversion. Temperature: 500 °C. Total pressure: 1 atm. Feed: C1 molar fraction: XC1 = 0.50, on Zn/H-ZSM-11(c) catalyst.

are available it is not possible the co-reactant molecules (C5–C6) were chemisorbed, i.e., at the C1 highest partial pressure. The adsorbed species react between them faster than the C1 and it would be the reason that C1 reach at the equilibrium before the C6.

3.4.3. Optimum performance envelopment technique

The optimum performance envelopment (OPE) technique allowed us to determine whether reaction products are primary, secondary, stable or unstable. Reaction conditions were the following: temperature 500 °C; C1 molar fraction, XC1 = 0.50; different contact time at TOS = 0. Figure 3 shows that C2–C2 = , C3 and C4 were present at initial stage of the reaction; the lowest C1 conversion levels indicated that they would be primary products from the C1 conversion. As C1 conversion increases, alkenes underwent secondary cracking, oligomerization and/or isomerization [19]. It could see that their yields pass through a maximum and then decrease, so they undergone a later transformation towards i-C4, C4 = and finally to yield AH.

Therefore, C4s production would be the intermediate step into the AH formation because of their yield diminish when C1 conversion still grow. The subsequent transformation allowed AH yield increase as high as 20%mol C in these conditions and would be the secondary and stable product of this complex mechanism of reaction. A careful analysis of the species evolution allowed understanding the C1 funtionalization mechanism using light gasoline co-reactant. Zn^{2+} function would be catalyzing C5 and C6 dehydrogenation. This dehydrogenation would occur by direct hydride abstraction that generates a surface carbenium-ion through an EDA (electron-donor-acceptor adduct), (14).
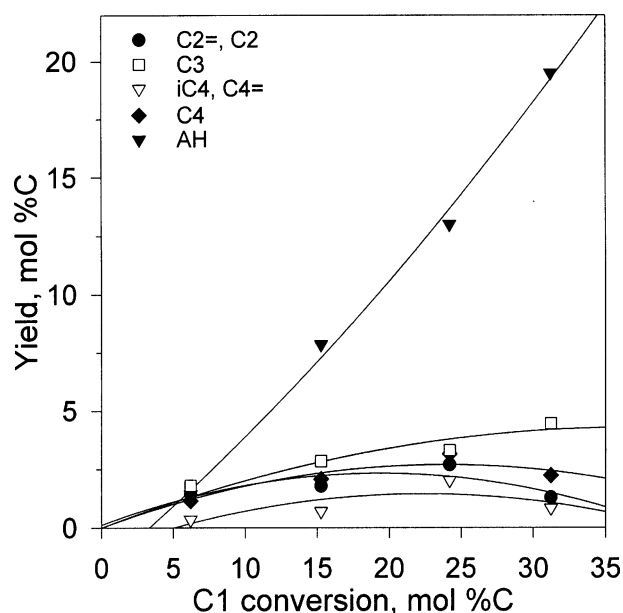
These species react to produce C2–C2 = , C3 and C4 then undergo a later transformation into C4 iso-alkanes and alkenes. Over this site would be where C1 molecule impact and incorporate in the fast alkene oligomerization and dehydrocyclization leading to naphthenic and aromatic products.

Is interesting to consider that the presence of strong Lewis acid sites (SLS) in the catalyst employed (table 1) prevents the alkenic intermediate hydrogenation and allow their efficient introduction into the complex mechanism towards aromatization. Meanwhile, the amount of Brönsted acid sites (both medium and strong) on the Zn/HZSM11(c) catalyst is low (see table 2) and thus the effectiveness of the cracking reactions by proteolysis of the adsorbed molecules is lower.

4. Conclusions

The number of Lewis sites increased by the incorporation of Zn^{2+} cations over the zeolitic material, allowed light gasoline compounds adsorption, pentanes as well as hexanes, to undergo the hydride abstraction to produce a surface ion carbenium-type intermediate capable to introduce the C1, from gas phase, into the aromatization mechanism.

Moreover, these sites are responsible to create dehydrogenation and aromatization centers which could explain the higher conversion levels of co-reactant compounds and AH yield. Furthermore, these sites showed a slow deactivation by coke in the reaction conditions. Thus, we found an effective methane activation using light gasoline (LG) as co-reactant over a Zn/HZSM-11, with conversions values as high as 50%

mol and 28% AH yield. These results have two goals: (a) the employ of natural gas (mainly C1) as source of more valued chemicals and (b) attractive advantage of the employing of light gasoline, which is a refinery cut with lower commercial value.

Acknowledgments

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