

Catalytic conversion of natural gas with added ethane and LPG over Zn-ZSM-11

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Abstract

The higher hydrocarbons (C₂₊) from natural gas (NG), such as ethane (C₂), propane (C₃) and butane (C₄) reached excellent levels of conversion over Zn-ZSM-11 at temperatures between 550–640°C and 1 atm total pressure, but the methane (C₁) present in NG could not be converted. The C₁ transformation by activation with co-reactants such as C₂ and liquefied petroleum gas (LPG), over Zn-ZSM-11 was studied. The addition of amounts of C₂ to a feed of commercial NG allowed to activate the C₁ reaching excellent values of conversion and yield to aromatic hydrocarbons (AH). The high Lewis/Bronsted sites ratio of Zn-ZSM-11 catalyst determined by pyridine desorption at different temperatures followed by FT-IR spectroscopy, allowed us to suggest that electron-donor–acceptor complex, formed between C₂₊ species and unoccupied molecular orbital of the zinc species present in the catalyst, favored the interaction of C₂₊ through carbenium intermediate to activate methane. ©2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Natural gas (NG) consists predominantly of methane (C₁) with relatively small amounts of ethane (C₂), propane (C₃) and higher paraffins. Large deposits of NG are found in many locations throughout the world. Not all the available and produced NG is utilized. At present, most of the NG is used as fuel and only in a few instances it is applied as a chemical feedstock. Modern industry supports a change of feedstock towards better and cheaper raw material [1]. Therefore, the direct conversion of C₁ to desirable commodity chemicals, such as liquid hydro-

carbons, is a challenging approach to the utilization of NG resources. C₁ conversion, under non-oxidizing conditions is a great task to catalysis science; consequently, considerable effort has been devoted to the development of novel catalytic systems. Lunsford et al. [2] studied the steady-state production of olefins in high yields from methane using an integrated recycle reaction system that includes a catalyst for the oxidative coupling reaction. Alternatively, the olefins may be converted to aromatics by using a Ga/H-ZSM-5 zeolite catalyst. Guzzi et al. [3] reported the non oxidative conversion of methane to larger hydrocarbons in a one-step process over Pt–Co/NaY bimetallic samples at low temperature. Mao-song et al. [4] studied the aromatization of methane without using oxidants. They proposed that this reaction on the Mo/ZSM-5

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zeolite catalyst is a structure-sensitive reaction and the deactivation of the catalyst is initially related to the reduction of the Mo species at higher valence and loss of surface oxygen. Wang et al. [5] and Pierella et al. [6] reported the aromatization of C1 in the presence of small amounts of light hydrocarbons under non-oxidizing conditions over Mo-MFI zeolite at low pressure (1–2 atm). At the moment, the direct activation of C1 from a feed of commercial NG has not been reported. Recently, Choudhary et al. [7] reported the aromatization of C2+ hydrocarbons present in NG over Ga-modified ZSM-5 type zeolite catalysts at different process conditions and atmospheric pressure but they informed negative values of C1 conversion. The catalysts ZSM-5 and ZSM-11 zeolites are currently of particular interest for aromatization of light paraffins. Modifications of zeolites with zinc or gallium have been successfully used for this purpose [8–13]. In previous papers, we have reported that Zn-ZSM-11 shows excellent aromatization behavior for ethane (C2), propane (C3), liquefied petroleum gas (LPG) and pentane (C5) [14–17]. The final purpose of this work is the transformation of C1 from NG into petroleum–chemical products. In a first instance, the aromatization of a pure NG feed has been investigated at different process conditions, over Zn-ZSM-11 catalyst. Then, taking into account these reactions results, we study the addition of co-reactants, such as C2 and LPG, to commercial NG feed over Zn-ZSM-11, in order to reach the direct C1 activation.

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 on-line gas chromatography equipped with a FID detector. The feeds used in this study were: commercial natural gas (C1 = 82.8; C2 = 16.1; C3 = 0.8; C4 = 0.3 mol%) supplied by ECO-GAS (Argentina), high purity methane (>99.97%) and ethane (>99.997%) supplied by AGA (USA) and LPG (C3 = 38.7, iC4 = 36.3, C4 = 25 mol%) supplied by YPF (Argentina). The studies with NG were carried out at GHSV(NG) between 1000–4000 cm³ g⁻¹ h⁻¹, temperatures between 550–640°C and times on stream

(TOS) between 30–170 min. The feeds C1 + C2 and C1 + LPG were evaluated at 550°C, GHSV (C2 or LPG) = 810 cm³ g⁻¹ h⁻¹ and C1 molar fraction 0.58 and 0.74, corresponding to GHSV (C1) = 1120 and 2300 cm³ g⁻¹ h⁻¹ respectively. The feeds NG + C2 were obtained by addition of 12 and 43% of C2 to NG, corresponding to a C1 molar fraction in the feed of 0.74 and 0.58, respectively, and were evaluated at 550°C and GHSV (C2) = 200–2200 cm³ g⁻¹ h⁻¹. After the addition of C2 into NG, the feed mixture comprised mainly C1 + C2 because the C3 + C4 molar fraction results were negligibly small (<0.009). Conversion and products distribution are expressed on a carbon-atom basis. ZSM-11 zeolite with a Si/Al ratio of (17) was synthesized by hydrothermal synthesis using tetrabutylammonium hydroxide (TBA) as template. The proton forms of the catalysts were prepared by ion exchange with 1 M ammonium chloride at 80°C for 40 h followed by 16 h calcination under nitrogen and 10 h under air. Zn zeolites were obtained by ion-exchange of NH₄⁺-zeolite with zinc nitrate solution (0.05 M, 80°C for 4–30 h). Zn-ZSM-11 with Zn²⁺/H⁺ molar fraction 0.86, 0.54, 0.45 and 0.24, was prepared. Infrared measurements were performed on a Nicolet 710 FTIR spectrometer. Samples were pressed into self supporting wafers (8–10 mg cm⁻²). Pyridine (3 Torr) was adsorbed at room temperature for at least 10 h, and desorbed for 2 h at 250, 350 and 400°C at 10⁻⁵ Torr. The number of Bronsted and Lewis sites was determined using the literature data on the integrated molar extinction coefficients [18], providing no dependence of the integrated coefficients on the catalyst or strength of the sites. We separated the strength of the sites in three regions: weak, medium and strong acid sites as a function of pyridine retained between 250–350°C, 350–400°C and above 400°C, respectively.

3. Results and discussion

3.1. Natural gas studies

3.1.1. Influence of space velocity

Results showing the influence of space velocity on the conversion of each NG component and on the products distribution over Zn-ZSM-11 at 550°C are

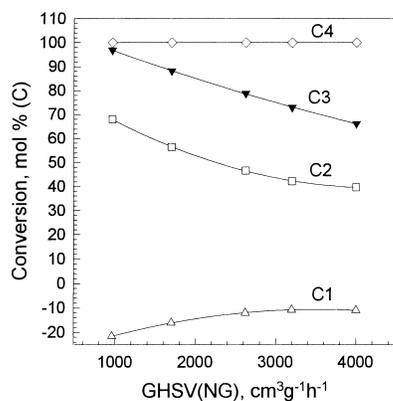


Fig. 1. Influence of the space velocity (GHSV (NG)) on the NG components (C1, C2, C3 and C4) conversion, over Zn-ZSM-11. Feed: NG, temperature: 550°C, TOS: 20 min, total pressure: 1 atm.

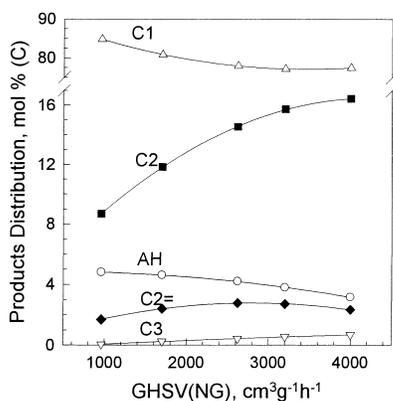


Fig. 2. Influence of the space velocity (GHSV (NG)) on the reaction products distribution, over Zn-ZSM-11. Feed: NG, temperature: 550°C, TOS: 20 min, total pressure: 1 atm.

presented in Figs. 1 and 2, respectively. The negative conversion of methane indicates its formation from higher hydrocarbons in the process. The C4 conversion was almost complete even at the high GHSV (NG) of $4000 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$. The C2 and C3 conversion decreased when GHSV (NG) increased. It is interesting to note that the C2 conversion at high GHSV (NG) is quite high (about 40%), despite its low reactivity. The AH production and C1 enhanced with decreasing GHSV(NG) whereas C2= decreased. Thus, the introduction of C2= intermediate into the aromatization process which produces aromatics and C1, is favored by the GHSV (NG) decrease.

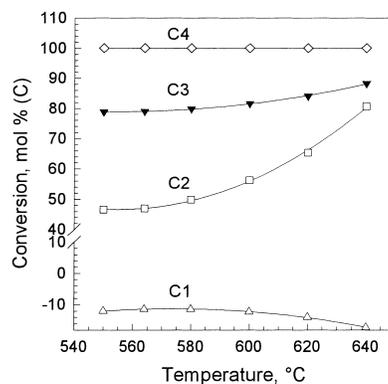


Fig. 3. Effect of the temperature on the NG components (C1, C2, C3 and C4) conversion, over Zn-ZSM-11. Feed: NG, GHSV (NG)= $2600 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$, TOS: 20 min, total pressure: 1 atm.

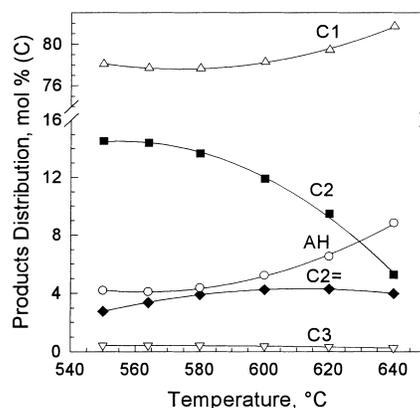


Fig. 4. Effect of the temperature on the reaction products distribution, over Zn-ZSM-11. Feed: NG, GHSV (NG)= $2600 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$, TOS: 20 min, total pressure: 1 atm.

3.2. Influence of temperature

Figs. 3 and 4 show the influence of temperature on the conversion of each NG component and on the products distribution, respectively, over Zn-ZSM-11 at GHSV (NG)= $2600 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$. Again, the C1 conversion was negative and C4 was completely converted at all the temperatures. As the temperature increased, the C3 conversion enhanced slightly whereas the C2 conversion increased appreciably reaching about 80% at 640°C. C2= was affected only to a small extent when the temperature increased whereas AH and C1 increased above 580°C. The aromatics reached 8% at

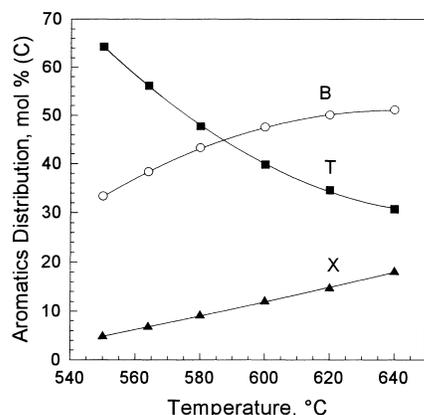


Fig. 5. Effect of the temperature on the aromatics distribution, over Zn-ZSM-11. Feed: NG, GHSV (NG) = 2600 cm³ g⁻¹ h⁻¹, TOS: 20 min, total pressure: 1 atm.

640°C. Thus, the aromatization process is also favored by the temperature.

It can be seen in Fig. 5 that the distribution of aromatics formed changes with increasing temperature. The relative concentration of benzene and xylenes increased whereas that of toluene decreases sharply. The amount of benzene and xylenes species at 640°C probably arises from demethylation and secondary transalkylation of the aromatic rings.

3.3. Influence of time on stream

The effect of time-on-stream on the conversion of each NG component and on the products distribution, respectively, over Zn-ZSM-11 at GHSV(NG) = 2600 cm³ g⁻¹ h⁻¹ and 550°C is shown in Figs. 6 and 7. It can be seen that C2, C3 and C4 conversion and aromatics distribution remains almost constant on the whole range of times-on-stream studied. It seems then that Zn-ZSM-11 would not be deactivated by coke deposition on active sites under the conditions used for the natural gas transformation.

All the above results show that C2+ hydrocarbons present in the NG can be converted over a Zn-ZSM-11 catalyst into more valuable products such as aromatics. The aromatization of C2+ hydrocarbons would occur simultaneously and a network of complex reactions such as dehydrogenation, cracking, oligomerization, cyclization and aromatization could succeed [7]. The trend for the influence of temperature and space velocity on NG conversion and products distribution

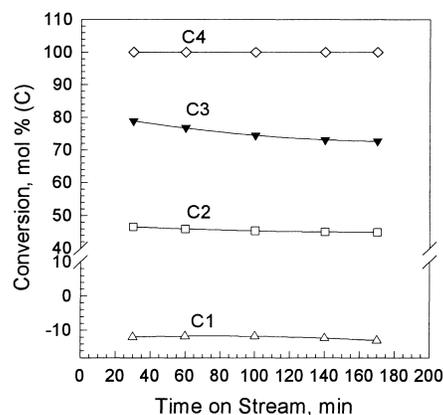


Fig. 6. Effect of the time on stream on the NG components (C1, C2, C3 and C4) conversion, over Zn-ZSM-11. Feed: NG, GHSV (NG) = 2600 cm³ g⁻¹ h⁻¹, temperature: 550°C, total pressure: 1 atm.

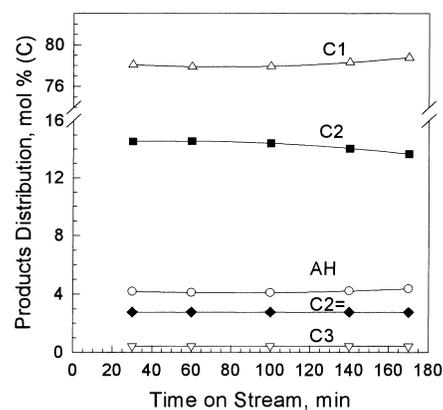


Fig. 7. Effect of the time on stream on the reaction products distribution, over Zn-ZSM-11. Feed: NG, GHSV (NG) = 2600 cm³ g⁻¹ h⁻¹, temperature: 550°C, total pressure: 1 atm.

reported here is consistent with the results of Choudhary et al. [7] although we obtained higher levels of C2–C3 conversion on Zn-ZSM-11 under similar experimental conditions but for a different NG feed. The negative values of C1 conversion indicate that the methane direct activation remained a challenging objective, which is discussed in the following sections.

3.4. Methane + ethane additive and methane + additive LPG studies

In Table 1 are presented the results obtained using C1 + C2 and C1 + LPG as feed over Zn-ZSM-11 zeo-

Table 1
Reaction^a results of C1 + C2 and C1 + LPG feeds, over Zn-ZSM-11 at the C1 molar fractions 0.58 and 0.74

	C1+C2		C1+LPG	
	0.58	0.74	0.58	0.74
Molar fraction C1	0.58	0.74	0.58	0.74
C1 Conversion (mol% C)	30.00	10.90	9.00	7.00
C2 Conversion (mol% C)	50.00	37.05	0.00	0.00
C3 Conversion (mol% C)	0.00	0.00	0.00	0.00
iC4 Conversion (mol% C)	0.00	0.00	90.00	85.00
C4 Conversion (mol% C)	0.00	0.00	32.00	9.00
Products distribution (mol% C)				
C1	30.00	51.57	25.16	40.98
C2	28.57	26.51	1.80	0.80
C2=	7.00	5.83	2.26	2.60
C3	4.00	0.39	23.25	17.97
iC4	0.00	0.00	2.91	3.37
C4	0.43	0.00	13.62	14.09
AH	30.00	15.70	31.00	20.19

^a Temperature: 550°C, GHSV (C2 or LPG): 810 cm³ g⁻¹ h⁻¹, TOS: 20 min, total pressure: 1 atm.

lite at different molar fractions of C1, space velocity GHSV (C2 or LPG) = 810 cm³ g⁻¹ h⁻¹ and at 550°C. Zn-ZSM-11 zeolite appears as a good material for C1 activation with C2 and LPG.

When the feed was C1 + C2, the C1 and C2 conversion increased sharply with decreasing C1 molar fraction and rise to excellent levels (30 and 50%, respectively) at C1 molar fraction 0.58. Thus, C1 could be activated by C2, initiating in this way its transformation [19,20]. Furthermore, according to reference [21], C2 was converted more efficiently in presence of C1 than in presence of N2 even at lower C2 molar fraction in the feed. C3 and AH yields increased as the C1 molar fraction diminished and AH reached 30% at C1 molar fraction 0.58. Thus, methane activation could proceed through the interaction with ethane (or ethyl-carbenium ions) toward aromatization steps. The strong Lewis acidic sites of the catalyst, such as an EDA complex, would allow this interaction [22,23].

When the feed was C1 + LPG, only C4 conversion increased significantly with decreasing C1 molar fraction whereas C1 and iC4 conversion showed a modest increase reaching 9 and 90% at C1 molar fraction 0.58. For both C1 molar fractions studied, the C3 conversion was zero which could be attributed to its lower reactivity than iC4 and C4 [24] as well as to its very low partial pressures in the feed (0.1 and 0.16 atm for C1 molar fraction 0.74

and 0.58, respectively). The iC4 appears as the LPG component more reactive, which would present the lowest activation energy to form the tertiary carbenium cation intermediates [24–26]. According to reference [27], the methane activation could occur through the interaction with iC4 because a direct relationship between the C1 conversion and the iC4 conversion can be observed. Furthermore, C1 and iC4 conversion would have reached the maximum levels for the reaction system equilibrium. As the C1 molar fraction decreased, AH enhanced, reaching 31% at C1 molar fraction of 0.58. The strong Lewis acid sites present in Zn-ZSM-11 as EDA adduct, would allow the interaction of reactive intermediates with C1 [22,23] and its introduction into the complex aromatization mechanism.

Although, LPG is able to activate C1 at higher C1 molar fraction in the feed than C2 [21,27], under the same experimental conditions, C2 appears to be more effective than LPG for the C1 activation. This finding could be attributed to the fact that the more reactive LPG components would present a much lower activation energy to react with other identical species than with C1 (chemically inert species). In addition, the numerous simultaneous reactions involved in the complex reaction pathway of methane and LPG (C3 + iC4 + C4) transformation can also produce methane, decreasing the neat conversion of this reactive.

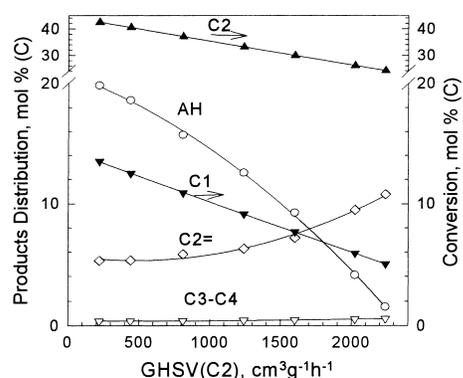


Fig. 8. Influence of the space velocity (GHSV(NG)) on the C1 and C2 conversion and on the reaction products distribution (AH, C2= and C3–C4), over Zn-ZSM-11. Feed: NG+C2 (12%), C1 and C2 molar fractions: 0.74 and 0.26, temperature: 550°C, TOS: 20 min, total pressure: 1 atm.

3.5. Natural gas + ethane additive studies

As can be seen in Figs. 1–7, the methane present in NG, where its molar fraction is 0.828, was not activated even at lower GHSV (GHSV (NG)=1000, GHSV (C2)=161 and GHSV (C1)=828 cm³ g⁻¹ h⁻¹) and higher temperatures (640°C) than those used in Table 1, in agreement with reference [7]. Thus, taking into account the results shown in the table, it seems reasonable that a addition of C2 into NG feed would allow to activate the methane.

Fig. 8 shows the influence of GHSV (C2) on the C1 and C2 conversion and the products distribution respectively over Zn-ZSM-11, when 12% of C2 was added to NG feed at 550°C. It can be seen that C1 (present in NG) would be activated by C2 [21] under these conditions. The C1 and C2 conversion enhances with decreasing GHSV (C2) reaching levels of 14 and 42%, respectively at GHSV (C2)=200 cm³ g⁻¹ h⁻¹. As GHSV (C2) decreases, C2=decreases whereas the aromatics increases significantly rising to 20% at GHSV (C2)=200 cm³ g⁻¹ h⁻¹. The C2= would appear as an intermediate species which would be consumed in the overall aromatization process as GHSV (C2) diminishes.

The influence of GHSV (C2) on the C1 and C2 conversion and the products distribution, respectively over Zn-ZSM-11, when 43% of C2 was added to NG feed at 550°C is shown in Fig. 9. C1 and C2 were converted to a greater extent under these new con-

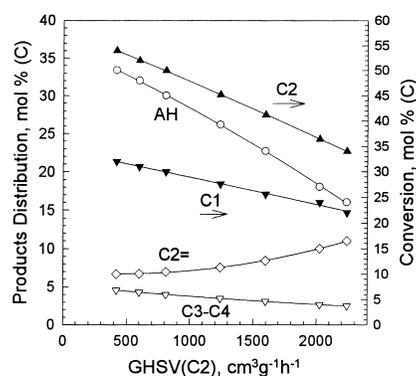


Fig. 9. Influence of the space velocity (GHSV(NG)) on the C1 and C2 conversion and on the reaction products distribution (AH, C2= and C3–C4), over Zn-ZSM-11. Feed: NG+C2 (43%), C1 and C2 molar fractions: 0.58 and 0.42, temperature: 550°C, TOS: 20 min, total pressure: 1 atm.

ditions rising levels of 33 and 56%, respectively at GHSV (C2)=200 cm³ g⁻¹ h⁻¹. The aromatics were the main products [21] in the whole range of GHSV (C2) studied, reaching a total of 35% at GHSV (C2)=200 cm³ g⁻¹ h⁻¹. As GHSV (C2) decreases, C2= would be introduced into the aromatization pathway and C3–C4 would appear also as result of the C1 (NG) activation with C2.

3.6. Relation between Zn-content and catalytic activity

Table 2 shows the data of infrared spectra of pyridine adsorbed on zeolite catalysts with different Zn content, allowing us to determine the concentration of Bronsted-acid sites and Lewis-acid sites. The concentration of pyridine interacting with Bronsted acid sites, PyH⁺ was calculated from the maximum intensity of the absorption at 1545 cm⁻¹. The adsorption band at 1450–1460 cm⁻¹ indicate the electron-donor–acceptor adduct EDA, of pyridine-Lewis sites in zeolites. The IR data for chemisorbed pyridine after adsorption at room temperature and after further outgassing the samples at 250, 350 and 400°C indicate that the number and strength of Lewis sites increases as Zn content and the Bronsted sites decreases.

In Fig. 10, we report the catalytic activity for a feed of NG plus 12% of ethane (C2 molar fraction=0.74 and GHSV (C2)=810 cm³ g h⁻¹) against the Zn

Table 2

FTIR data of the weak, medium and strong acid sites as a function of pyridine retained between 250–350°C, 350–400°C and above 400°C, respectively on H-ZSM-11 zeolites with different zinc content

Catalyst	FTIR ^a Py (μmol/g)					
	WBS	MBS	SBS	WLS	MLS	SLS
H-ZSM-11	74	94	79	7	5	1
Zn-H-ZSM-11 ^b	24	51	22	146	108	243
Zn-H-ZSM-11 ^c	41	65	41	95	74	158
Zn-H-ZSM-11 ^d	47	71	49	76	56	127
Zn-H-ZSM-11 ^e	59	81	63	41	31	70

^a WBS: weak Bronsted sites; MBS: medium Bronsted sites; SBS: strong Bronsted sites; WLS: weak Lewis sites; MLS: medium Lewis sites; SLS: strong Lewis sites.

^b 0.86 ($Zn^{2+}/Zn^{2+} + H^+$ molar fraction).

^c 0.54 ($Zn^{2+}/Zn^{2+} + H^+$ molar fraction).

^d 0.45 ($Zn^{2+}/Zn^{2+} + H^+$ molar fraction).

^e 0.24 ($Zn^{2+}/Zn^{2+} + H^+$ molar fraction).

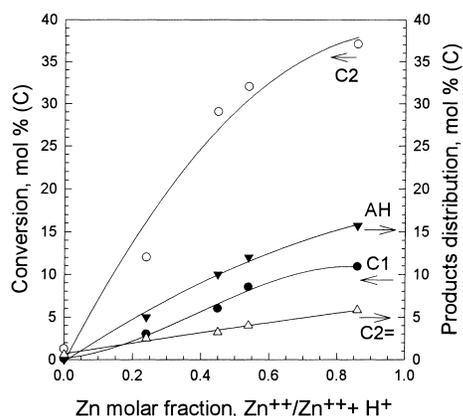


Fig. 10. Influence of Zn content on catalytic activity of ZSM. Feed: NG+C2 (12%), C1 molar fraction: 0.74, GHSV (C2): $810\text{ cm}^3\text{ g}^{-1}\text{ h}^{-1}$, temperature: 550°C , TOS: 20 min, total pressure: 1 atm.

content. As can be seen, the C1 and C2 conversion, and C2= and aromatic hydrocarbons increase as the Zn content increases.

4. Conclusions

The NG, used in this study, with C1 molar fraction of 0.828 can be converted into aromatics over Zn-ZSM-11 at $550\text{--}640^\circ\text{C}$, GHSV (NG) = $1000\text{--}4000\text{ cm}^3\text{ g}^{-1}\text{ h}^{-1}$ and 1 atm total pres-

sure. These products would proceed from higher hydrocarbons (C2+) from NG taking into account that the negative values of C1 conversion was obtained. In order to activate C1 from NG, C2 and LPG was evaluated as co-reactants and C2 resulted more efficient for this purpose. The C1 conversion reached levels of 14 and 33% by addition of 12 and 43% of ethane to a commercial NG feed, respectively. We suggest that Zn-ZSM-11 catalyst allowed the C1 activation by interaction between reactive intermediates-Lewis acid sites of catalyst and C1. The aromatics are the main products of this interaction and would appear as result from a complex network of simultaneous reactions such as dehydrogenation, oligomerization, cracking, cyclization, dealkylation and aromatization.

Acknowledgements

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