

Improvement of methane activation using *n*-hexane as co-reactant over Zn/HZSM-11 zeolite

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Abstract

Significance of effective conversion of methane (C_1) to more valuable compounds such as aromatics is studied using *n*-hexane (C_6) as co-reactant. AH yield was as high as 30 mol% C using the following reaction conditions: temperature, 500 °C; contact time $w/f = 30 \text{ g h mol}^{-1}$ and a C_1 molar fraction, $X_{C_1} = (C_1/C_1 + C_6) = 0.60$, was achieved. The effect of the contact time, molar fraction, and time on stream was analyzed in order to obtain more information about different species evolution. The C_1 conversion reached at 50 mol% C using Zn/HZSM-11 with 2.13 mol Zn per cell unit.

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1. Introduction

Catalytic conversion of methane (C_1) to the major aromatic building blocks as such as benzene, toluene and xylenes (BTX) is a huge challenge not only for the potential utilization of natural gas, because its very low value and large reserve volume, but to challenge catalytic science.

Direct conversion of methane was firstly developed using an oxidative couple because of alkane inertness but the main products were from total oxidation of methane (H_2O , CO and CO_2), thermodynamically more favorable than the direct transformation of methane into aromatics [1,2]. Medium-pore pentasil zeolites, mainly ZSM-5 and ZSM-11 modified with transition metal cations [3,4], that have been successfully used for this purpose and were more active and more selective than the ZSM zeolites in H-form [5]. Wang et al. [6] and Pierella et al. [7] reported that methane could be dehydrocyclized to aromatic hydrocarbons in presence of light hydrocarbons under non-oxidative conditions, and

lower temperature (500–700 °C) over Mo/H-ZSM5 catalyst at low pressure (1–2 atm). Aromatization of natural gas over H-Ga-MFI, H-GaAl-MFI and Ga/H-ZSM5 zeolite catalysts has been investigated at different process conditions by Choudhary et al. [8], indicating that the major fraction of the C_{2+} from natural gas can be converted to aromatics with high selectivity, depending the catalysts and process conditions employed. There is a general agreement about the catalytic role of the Zn or Ga cations in order to enhance the dehydrogenation and dehydrocyclization process involved as key steps in the conversion of alkanes to aromatics [9,10]. In this work, we report new results using in feedstock *n*-hexane ($n-C_6$) instead of *n*- C_5 improving the later performance, towards our target.

2. Experimental

The catalysts preparation and characterization and the catalytic system employed in the $C_1 + C_6$ conversion were described elsewhere [11]. 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/

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Table 1

Catalytic activity for $C_1 + C_6$ conversion and FTIR characterization of the used samples

Catalysts ^a	$C_1 + C_6^b$		FTIR ^c ($\mu\text{mol g}^{-1}$)					
	C_1 conversion	C_6 conversion	350–200 °C		400–350 °C		>400 °C	
			BS	LS	BS	LS	BS	LS
Zn/HZSM-11(a)	1.17	89.50	47	76	71	56	49	127
Zn/HZSM-11(b)	14.27	92.49	41	95	65	74	41	158
ZnHSM-11(c)	18.11	93.25	24	146	51	108	22	243
HZSM-11	11.64	86.41	93	7	79	5	74	1

^a ICP analysis for the samples (a), (b) and (c): Si/Al 17; mol Zn/cell unit = 0.54, 1.33 and 2.13, respectively.^b Mol% C. Reaction conditions: w/f ($n\text{-C}_6$) = 15 g h mol⁻¹. Feed: $C_1 + n\text{-C}_6$, C_1 molar fraction $X_{C_1} = 0.60$; TOS = 20 min; 500 °C; total pressure 1 atm.^c Pyridine retained at different temperature and at 10⁻⁴ Torr for 4 h. BS: Bronsted sites; LS: Lewis sites.

cell unit, respectively (Table 1). Feedstocks used in this study were: high-purity methane (>99.97% w/w) supplied by AGA and n -hexane (99.5% w/w) supplied by Aldrich. The reactions were carried out first, using $N_2 + n\text{-C}_6$ as feed at different contact time, w/f ($n\text{-C}_6$) = 1.5–30 g h mol⁻¹ and time on stream, TOS: 20–130 min, and a constant molar fraction of $N_2 = 0.60$. Then, C_1 was used instead of N_2 at the following reaction conditions: methane molar fraction, $X_{C_1} = (C_1 / C_1 + n\text{-C}_6)$ from 0.3 to 0.7, at a constant temperature of 500 °C and different contact time, w/f ($n\text{-C}_6$) = 1.5–30 g h mol⁻¹ and time on stream TOS: 20–130 min. Conversion, selectivity and yield to reaction products were expressed on molar carbon atom basis.

3. Results and discussion

3.1. Influence of the Zn content

Zn-ZSM-11 with varying amounts of Zn we used to test the catalyst performance for the activation of methane (C_1) using n -hexane (C_6) as co-reactant to produce aromatic hydrocarbons with the least amount of side products. According to the data showed in Table 1, the C_1 conversion increases as the zinc content increases.

In order to determine the strength and nature of the active sites additional studies of FTIR were performed using pyridine as probe molecule. According to these results and the C_1 conversion from each sample (Table 1), methane activation is strongly influenced by the nature and concentration of the active sites on the catalysts by the introduction of Zn^{2+} as counter ion, generating new and strong Lewis sites. The best results were obtained with sample (c), so in the further studies, to determine the influence of different reaction parameter, we choose sample (c).

3.2. $N_2 + n\text{-C}_6$ studies

To analyze methane (C_1) formation from $n\text{-C}_6$ conversion, nitrogen (N_2) as an inert gas was added into the

feed at a constant molar fraction, $X_{N_2} = N_2 / N_2 + n\text{-C}_6$ of 0.60 and contact time of $n\text{-C}_6$ from 1.5 to 30 g h mol⁻¹, 500 °C and atmospheric total pressure. As shown in Fig. 1, $n\text{-C}_6$ conversion increases with the contact time; showing that reaction has not reached to the equilibrium state even at higher w/f as 30 g h mol⁻¹. On the other hand, C_1 and aromatic hydrocarbons (AH) yields increase continuously up to 40 and 3 mol%, respectively, at the highest contact time (30 g h mol⁻¹). Meanwhile, light hydrocarbons $C_2\text{--}C_4$ (ethene, ethane, iso-butane, butene, butane) begin to be formed even at low conversion levels and their yield go through a maximum (about 15–20 g h mol⁻¹) and decrease at higher conversion levels, showing a secondary transformation. These results suggest that increasing the contact time, the reaction intermediates undergone aromatization, conducting reactions which prevails over 15 g h mol⁻¹, so the terminal cracking activity decreases when the contact time increases and then becomes lower than the scission in C_2 and/or C_3 carbons. Therefore, AH are formed as the C_4 s start to consume, so AH are the main secondary and stable products from $n\text{-C}_6$ as can see in

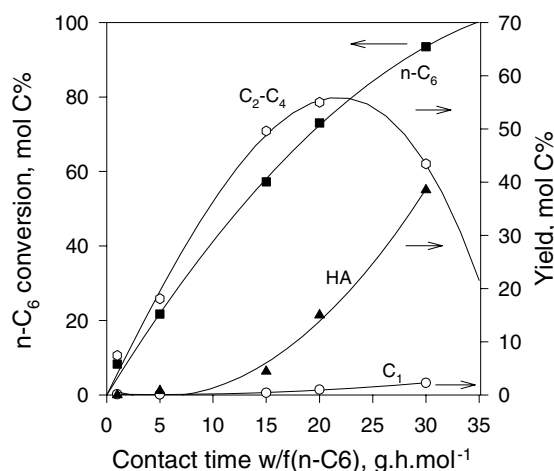


Fig. 1. $n\text{-C}_6$ conversion, and C_1 , $C_2\text{--}C_4$ light hydrocarbons and AH yields vs. contact time w/f ($n\text{-C}_6$). Feed $N_2 + n\text{-C}_6$, molar fraction $X_{N_2} = 0.60$; TOS = 0 min; 500 °C; total pressure 1 atm.

Section 3.4, Fig. 5 when the feed is $C_1 + n\text{-C}_6$. Methane is other secondary product that appears during the aromatic formation and grows constantly with the contact time of $n\text{-C}_6$. The C_1 yield reached to 3 mol%. Thus, as the next results indicate, the C_1 production from $n\text{-C}_6$ transformation is insignificant, and has to be considered in the following studies using $C_1 + n\text{-C}_6$.

3.3. $C_1 + n\text{-C}_6$ studies

3.3.1. Methane partial pressure effect

C_1 partial pressure effect was studied at $n\text{-C}_6$ contact time = 30 g h mol⁻¹; temperature = 500 °C and 1 atm of total pressure. When methane molar fraction is equal to 0, the $n\text{-hexane}$ conversion reached to 89.7 mol% and the main products were: methane (11.3 mol%), ethane–butanes (37.8 mol%), pentanes (8.7 mol%) and aromatic hydrocarbons (32.5 mol%). In the same way, Fig. 2 shows the effect of molar fraction of C_1 from 0.3 to 0.7. At lower and medium C_1 molar fraction (or partial pressure), its conversion increases from 30 to 50 mol% with the increasing of its molar fraction, the $n\text{-C}_6$ conversion is not affected by the variation of the C_1 molar fraction in the feed, with a practically constant yield (90 mol%). Above of $X_{C_1} = 0.60$, the conversion of the reactants decreases. It can be seen, that light hydrocarbons ($C_2\text{--}C_4$) yields also were constant, whereas AH are the main reaction products at lower and medium C_1 partial pressure, reaching as high as 40 mol%. The highest initial $n\text{-C}_6$ conversion indicates that $n\text{-C}_6$ is the first molecule to achieve the active sites to be transformed into intermediates species. Meanwhile, the maximum in the C_1 conversion suggests that it is a function of the nature of the ad-species in the $n\text{-C}_6$ transformation. At lower partial pressure of $n\text{-C}_6$, a minor proportion of C_6^+ or its intermediates ad-species

decrease; it induces a diminution in C_1 conversion. At higher $n\text{-C}_6$ molar fraction, the intermediate species react between them, taking account the lower partial pressure of C_1 . From these results, it is possible to suppose that the reaction mechanism would be a Rideal type, where C_1 impact from gas phase to $n\text{-C}_6$ active species adsorbed onto Zn^{2+} sites (carbenium-ion species formed by hydride abstraction of the Lewis sites of the catalyst).

3.3.2. Influence of time-on-stream

In Fig. 3 $n\text{-C}_6$ and C_1 conversion and yields to AH and $C_2\text{--}C_4$ light hydrocarbons data for $C_1 + n\text{-C}_6$ reaction over Zn/HZSM-11 (sample c) are plotted against time-on-stream, at 500 °C, C_1 molar fraction $X_{C_1} = 0.60$, contact time w/f ($n\text{-C}_6$) = 30 g h mol⁻¹ and reaction time between 20 and 190 min. Firstly, as shown in Fig. 3, C_1 conversion decreases more quickly than $n\text{-C}_6$ conversion as the time-on-stream increases, indicating that, $n\text{-C}_6$ is transformed to other reaction products without interaction with C_1 . It can be suggested that Zn/H ZSM-11 would be deactivated as the TOS increases, supporting the reaction mechanism above suggested. At higher time-on-stream the deactivation would occur over active sites for intermediate ad-species which can activate C_1 .

Aromatic hydrocarbons are the main reaction products (30 mol%) at lower TOS, however, when the aromatics begin to decrease (higher TOS), the light hydrocarbons $C_2\text{--}C_4$ (ethane, ethene, propane and butanes) increase, reaching to a maximum. These data showed that the catalyst deactivation favors the cracking path-way over the cyclization and aromatization. At higher reaction time (150 min) light hydrocarbons begin to decrease. Thus, the sites of the catalyst remain active and selective towards AH (although its production is 25

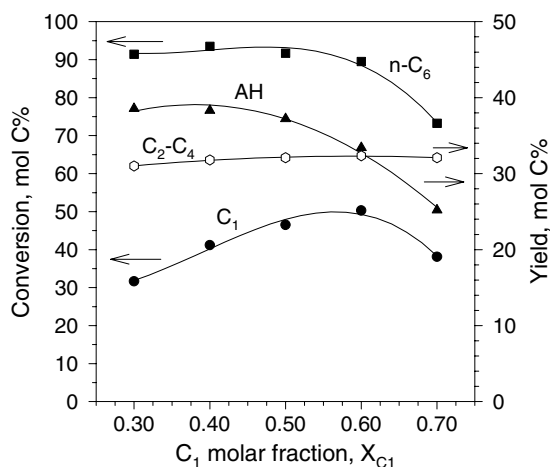


Fig. 2. $n\text{-C}_6$ and C_1 conversion, $C_2\text{--}C_4$ light hydrocarbons and AH yields vs. C_1 molar fraction. Feed $C_1 + n\text{-C}_6$; TOS = 20 min; 500 °C; total pressure 1 atm.

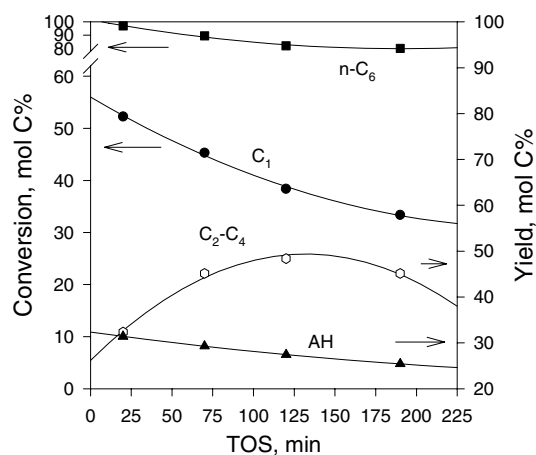


Fig. 3. $n\text{-C}_6$ and C_1 conversion, $C_2\text{--}C_4$ light hydrocarbons and AH yields vs. reaction time TOS. Feed $X_{C_1} = 0.60$; 500 °C; total pressure 1 atm.

mol%) even at the highest contact time (30 g h mol^{-1}) and higher TOS.

The acceptor electron sites (Lewis sites generated by the zinc loaded) are very active to lead the reaction intermediates towards aromatization, and very slowly deactivated by coke deposition in the reaction condition studied in this work.

3.3.3. Effect of contact time

The activation of C_1 with $n\text{-C}_6$ as co-reactant, over Zn/H-ZSM11 sample (c), using a C_1 molar fraction $X_{C_1}=0.60$, at 500°C , atmospheric pressure, and different $n\text{-C}_6$ contact time is shown in Fig. 4. $n\text{-C}_6$ and C_1 conversion increases as the w/f ($n\text{-C}_6$) increases in the whole range of contact time studied. The main reaction products are the aromatic ones. However, C_1 conversion reaches to the equilibrium more quickly than $n\text{-C}_6$ conversion. It would be other evidence of Rideal type interaction. The Zn loaded as a counter-ion on the surface of the catalyst, generates Lewis active sites to adsorb $n\text{-C}_6$ molecules by hydride abstraction which are transformed into very reactive intermediate species as olefins or naphthenics. Over these intermediates species, methane could impact from gas phase to be activated. When C_1 partial pressure is equal to 0.60, the coverage of the active sites for $n\text{-C}_6$ is medium, too, generating ad-species such as C_{2+} , and methane can reacts with these intermediate species with high efficiency. Nevertheless, when only some unused single sites exist and they are not easy available for chemisorbing a molecule of $n\text{-C}_6$ (higher molar fraction of C_1) the intermediate species interact between them, more quickly than with methane, so C_1 reached the equilibrium in its conversion before $n\text{-C}_6$.

It can be seen that light hydrocarbons as $C_2\text{--}C_4$ remained almost constant (5 mol%) at whole the range of

contact time studied, whereas the AH are the mainly reaction products, showing the effectiveness of the aromatization pathways over the cracking ones.

3.4. Application of OPE technique

We applied the standard optimum performance envelope technique OPE, as a tool that allowed us to determinate primary, secondary, stable or unstable reaction products. For this study we choose the following operating conditions: temperature 500°C ; C_1 molar fraction, $X_{C_1}=0.60$ and different $n\text{-C}_6$ contact time and at TOS = 0.

As was shown in Fig. 5, $C_{2=}$ and C_{4s} are primary and unstable reaction products, whereas $C_2\text{--}C_3$ are primary but stable ones. AH appear as secondary reaction products, increasing as the C_1 conversion increases indicating that they are stables. The evolution of the different species have been analyzed to understand the higher activation of C_1 obtained with the Zn-containing zeolite and $n\text{-C}_6$ as co-reactant.

The function of Zn^{2+} species would be the dehydrogenation of $n\text{-C}_6$ by the direct abstraction of a hydride producing a carbenium-like surface species through electron-donor-acceptor adducts (EDA) formation. Then, these species react in order to produce intermediates as C_3 and C_4 and more reactive olefins ($C_{2=}$, $C_{4=}$) and latter isoparaffin ($i\text{-C}_4$). The carbenium ad-species formed from them interact with C_1 producing its transformation to naphthenic and aromatics.

It is interesting to observe, that the presence of strong Lewis sites (SLS) on the catalyst (Table 1) prevents the hydrogenation of intermediate alkenes, which would be

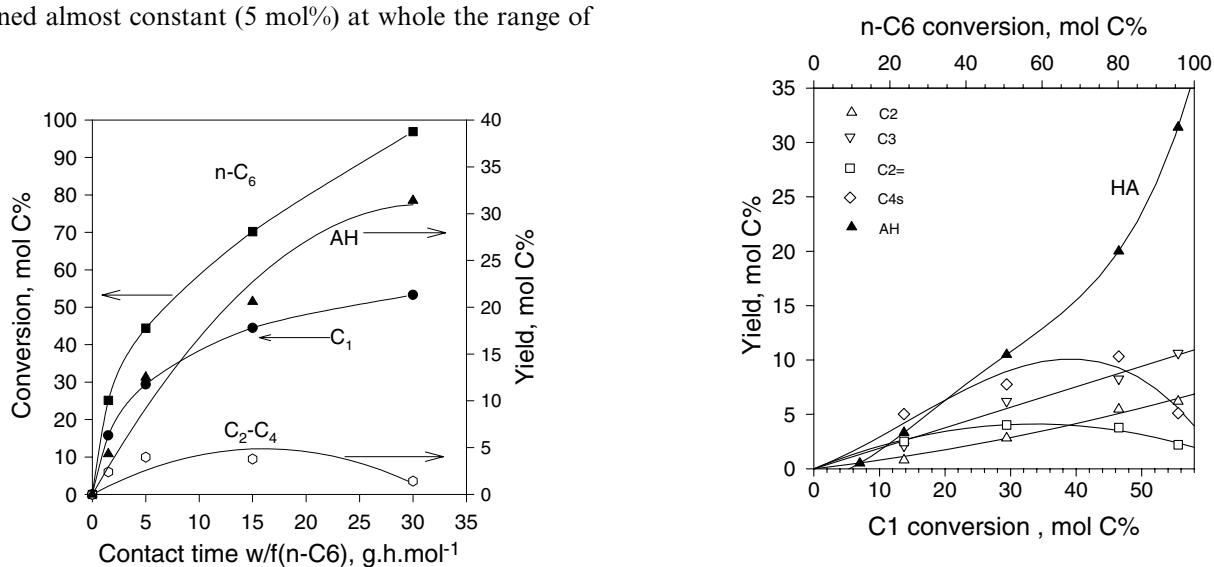


Fig. 4. $n\text{-C}_6$ and C_1 conversion, $C_2\text{--}C_4$ light hydrocarbons and AH yields vs. contact time w/f ($n\text{-C}_6$). Feed $C_1 + n\text{-C}_6$, molar fraction $X_{C_1}=0.60$; TOS = 0 min; 500°C ; total pressure 1 atm.

Fig. 5. $C_2\text{--}C_4$ light hydrocarbons and AH yields as function of the C_1 and $n\text{-C}_6$ conversion. Feed $C_1 + n\text{-C}_6$, C_1 molar fraction $X_{C_1}=0.60$; w/f ($n\text{-C}_6$): $1.5\text{--}30 \text{ g h mol}^{-1}$ TOS = 0 min; temperature: 500°C ; total pressure 1 atm.

efficiently introduced into polymerization, cyclization, dehydrogenation and aromatization complex mechanism. The higher activation of C₁ is due to the low effectiveness of the catalyst to crack *n*-C₆ by proteolysis, according to the low proportion of Brönsted acid sites.

4. Conclusions

The nature and concentration of the active sites on the HZM-11 catalyst (Zn²⁺ species) are essential for the effective methane incorporation into the complex reaction mechanism towards the aromatization. Thus, the number of Lewis sites increased by the introduction of Zn cations over the zeolitic material allowing the adsorption of *n*-hexane and then by hydride abstraction the formation of carbenium surface ion intermediate, capable of introduce the C₁ into the aromatization mechanism. These sites are also responsible for the creation of dehydrogenation and aromatization centers which explain the high levels of *n*-C₆ conversion and aromatic hydrocarbon yield. Thus, we report the effectiveness of C₁ activation using *n*-C₆ as co-reactant over Zn/HZSM-11 zeolite, reaching at a high conversion as 50.3 mol% and aromatics yield upper than 30 mol%.

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