

# 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  $w/f = 30 \text{ g h mol}^{-1}$  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  $\text{CO}_x$  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 ( $C_8$ ) = 1.5% w/w) [1], liquefied petroleum gas (LPG) ( $C_3$  = 38.7,  $iC_4$  = 36.3, and  $C_4$  = 25.0 mol%) [2], and natural gas (constituted by methane (C1) = 82.8,  $C_2$  = 16.1, and  $C_3$ – $C_4$  = 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 ( $C_2$ ), propane ( $C_3$ ), 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  $\text{N}_2 + n\text{-C5}$  as feed at different molar fractions of  $\text{N}_2$ , 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  $\text{N}_2$  under the following reaction conditions: methane  $XC1$  ( $= C1/(C1 + n\text{-C5})$ ) from

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