

Letter

Aromatization of methane over Mo/H-ZSM-5 catalyst: on the possible reaction intermediates

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Received 6 August 1998; received in revised form 13 October 1998; accepted 19 November 1998

Abstract

Methane aromatization has been performed on 4 wt.% Mo/H-ZSM-5 (Si/Al = 26). Acetylene has been observed as an intermediate and the change in the acetylene concentration as a function of contact time strongly suggested that the aromatization of methane is occurring via acetylene. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Aromatization; Methane; Acetylene

It has been reported by several groups [1–3] that, at high temperature (600–800°C), molybdenum loaded H-ZSM-5 is active for the selective aromatization of methane into benzene and naphthalene.

It has been shown that at the initial stage of the reaction large amount of hydrogen was formed with the consecutive formation of Mo₂C from MoO₃ [2]. It was suggested that Mo₂C is the active component for the methane activation and transformation into C₂H₄. Aromatization occurred through C₂H₄ oligomerisation/cyclisation reaction catalyzed by protonic acid sites; thus, Mo loaded H-MFI apparently acts as a bifunctional catalyst [1–3].

It is worthwhile to point out that the aromatic distribution is strongly in favour of benzene. Solymosi et al. [3] measured a benzene/toluene

ratio of 16, value close to that reported by Shu et al. [1].

Indeed it is expected that high temperature will favour benzene among aromatics but this could also suggest the possible existence of another reaction pathway. For this reason, we have re-investigated the reaction of methane over MoO₃/H-ZSM-5 catalyst. H-MFI (Si/Al = 26, Sud Chemie, Germany) was used as a support and the molybdenum loading was 4 wt.% (MoO₃ basis), the MoO₃ precursor being ammonium molybdate (Strem Chemicals). The Mo salt in water was deposited on the support by wetness impregnation technique and after being dried at 100°C overnight, the catalyst was calcined at 750°C for 12 h under an oxygen flow. The reaction was studied by using a microflow reactor. Reactant and products were analyzed by using in line two chromatographs equipped with Bentone and Unibed columns (Altech France) for hydrocarbons and one

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catharometer chromatograph with a Silica Gel Column (Altech France) for H_2 analysis.

The reaction was performed at 750°C , the reactor being fed with methane at atmospheric pressure. In Fig. 1 are reported the conversion of methane and the selectivity into benzene (carbon basis) as a function of time on stream.

It is observed that the benzene selectivity is increasing with TOS, these results being in good agreement with those reported earlier [1–3]. On the chromatograph equipped with the Unibed Colum (analysis of light hydrocarbons), in addition to the peaks due to C_2H_4 and C_2H_6 a small unidentified peak was observed. To identify this product, all products were collected in a cold trap (acetone dry ice bath) and GCMS experiments were performed: this small peak was identified as due to acetylene. Thus, it appears that C_2H_2 was in addition to C_2H_4 produced from the reaction of methane. In order to investigate whether acetylene is a primary reaction product, the contact time was varied. Results are reported in Fig. 2. It must be pointed out that the scales for benzene, ethylene and for acetylene are much different, acetylene being in minor concentration compared to ethylene. The interesting point is that acetylene pressure increases when contact time decreases while the opposite is observed for ethylene and benzene; this observation suggests that acetylene could be the primary product whereas C_2H_4 and C_6H_6

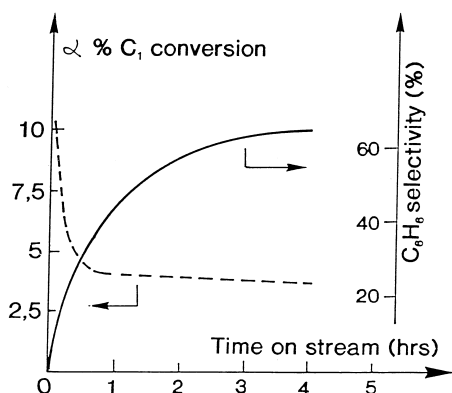


Fig. 1. Conversion of methane over 4 wt.% Mo/H-ZSM-5. $T = 750^\circ\text{C}$. Change in methane conversion and benzene selectivity with time on stream.

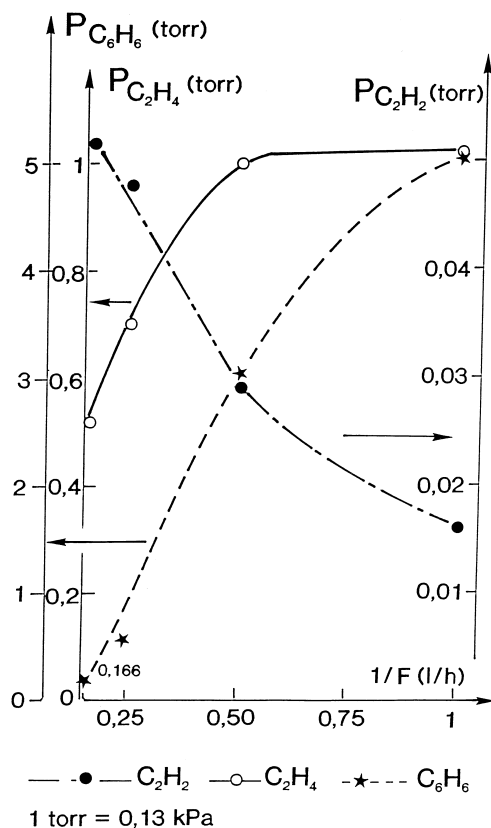


Fig. 2. Conversion of methane over 4 wt.% Mo/H-ZSM-5. $T = 750^\circ\text{C}$. Change in product distribution as a function of flow rate. F: flow of reactant. (●) C_2H_2 , (○) C_2H_4 , (×) C_6H_6 .
1 torr = 0,13 kPa

exhibit the behaviour, with respect to the contact time, of secondary products.

These results possibly suggest that an alternative reaction mechanism could be proposed. Previous works have mentioned that ethylene is the primary product because “its selectivity was observed to increase with increasing reaction space velocity, while those of all other products simultaneously decrease” [2]. Indeed, such a conclusion can also be derived from the examination of results reported in Fig. 2 when acetylene is not taken into consideration but this is no more true when all products, including C_2H_2 , are considered.

These results suggest that C_2H_2 could be the primary product.

Indeed, it has been checked by flowing a mixture of acetylene and nitrogen (1% of

acetylene, 99% N₂) over Mo/H-ZSM-5 that the product distribution is very close of that obtained when feeding with ethylene + N₂. Details will be reported in a coming paper.

The suggestion that C₂H₂ could be the primary product from methane reaction over Mo₂C/H-ZSM-5 throws a different light on the reaction mechanism.

Upon reaction of CH₄ over Mo₂C dehydrogenation occurs with the subsequent formation of CH₃, CH₂, CH fragments, CH being the most favourable for C₂H₂ formation.

C₂H₂ so formed may be hydrogenated over Mo₂C into C₂H₄ or may be trimerized into benzene over Mo₂C or over Brönsted acid sites of the MFI support.

In conclusion, this work provides a tentative mechanism for the homologation of methane into benzene when CH₄ is converted into acetylene and hydrogen. The role of H⁺ in the

overall CH₄ reaction remains unclear. Studies are in progress to identify the exact role of H⁺ in the activation of methane and in the formation of aromatics.

Acknowledgements

Dr. Nicolai (CPE, University of Lyon 1) is acknowledged for having identified C₂H₂ by GCMS. Total Raffinage Distribution is acknowledged for his funding.

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