

# Aromatization of methane over zeolite supported molybdenum: active sites and reaction mechanism

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## Abstract

The conversion of methane to aromatics, mainly benzene, has been studied. Zeolite type catalysts, ZSM-5, MCM-22, containing molybdenum were used. The reaction was carried out at 973–1073 K and atmospheric pressure. Aromatics were formed after an induction period during which molybdenum carbide was formed. Induction period was followed by analyzing infrared (IR) band of the acidic OH. Zeolite plays an important role for increasing Mo dispersion. Comparison between ZSM-5 and MCM-22 showed that Mo/MCM-22 was twice more active than Mo/ZSM-5. This was attributed to more open topology of MCM-22 which facilitated the migration of Mo ions towards exchangeable positions thus favoring Mo dispersion, and also reduced diffusion limitation of the aromatic products. Analysis of the products at high space velocity showed that acetylene was formed as primary product along with possibly ethylene. Acetylene was converted into aromatics (benzene, naphthalene) as the space velocity decreased. IR analysis in the OH stretching vibrations showed that H<sup>+</sup> ions, in H-ZSM-5, are progressively exchanged during the calcination of Mo/HZSM-5, and almost completely removed after the induction period following CH<sub>4</sub> reaction at 823 K. At high temperature in O<sub>2</sub> molybdenum species, possibly MoO<sub>2</sub><sup>+</sup> (Mo<sub>2</sub>O<sub>5</sub>)<sup>2+</sup>, migrate in the zeolite framework and replace H<sup>+</sup>. These species were further converted into Mo<sub>2</sub>C by reaction with methane, residual carbon species (coke) poisoning the residual zeolite protons. The reaction of CH<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> over acidic H-ZSM-5, H<sup>+</sup> poisoned Mo<sub>2</sub>C/H-ZSM-5 and non-acidic Mo<sub>2</sub>C/SiO<sub>2</sub> was studied. It resulted that H<sup>+</sup> sites are not prerequisite for aromatization of C<sub>2</sub>H<sub>2</sub> or C<sub>2</sub>H<sub>4</sub>. It was concluded that the principal route for the aromatization of CH<sub>4</sub> is the formation of C<sub>2</sub>H<sub>2</sub> over Mo<sub>2</sub>C which again over the molybdenum carbide forms benzene. The bifunctional mechanism apparently was less important. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Methane aromatization; Molybdenum; ZSM-5; MCM-22

## 1. Introduction

The direct catalytic conversion of methane into aromatics and hydrogen is an interesting route for upgrading natural gas. Recently, it has been shown that supported molybdenum, preferentially Mo supported on H-ZSM-5, are active and selective for benzene

formation from methane [1–4]. It was clearly established that at high temperature under CH<sub>4</sub> molybdenum in Mo/HZSM-5 was reduced and formed Mo<sub>2</sub>C species [5] and further during the activation process of Mo/HZSM-5 molybdenum species migrated towards exchangeable sites in the zeolite framework [5,6]. It is generally reported that the activation of methane occurs on molybdenum active species forming ethylene as primary product C<sub>2</sub>H<sub>4</sub> being converted into benzene

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over  $H^+$  acid sites of the zeolite [1–6]. In a very recent work it was shown by contrast that acetylene was the primary product of the reaction of methane over Mo/HZSM-5 [7], and the authors concluded that a possible route for the formation of benzene is the production of  $C_2H_2$  on Mo sites, acetylene generating at high temperature benzene and naphthalene.

The aim of this work was to provide an integrated understanding on the nature of active sites operating during the aromatization of methane over Mo/H-ZSM-5 catalyst. The role of the zeolite will be examined by comparing H-ZSM-5 and H-MCM-22 having different topology. The role of protons in the zeolite, in which protons apparently improved the catalytic performances, will be examined, and a reaction mechanism proposed.

## 2. Experimental

### 2.1. Catalysts

H-ZSM-5 zeolite (Si/Al = 26 batch 1381 from Süd Chemie Germany) was impregnated with an aqueous solution of ammonium heptamolybdate. The sample was dried and then calcined in air at 773 K. The Mo loading was adjusted to 4 wt.%. In addition a series of Mo/H-ZSM-5 catalysts were prepared by the same procedure but using H-ZSM-5 zeolites with different Si/Al ratio synthesized in the laboratory. Mo loading was also 4 wt.%.

H-MCM-22 was synthesized as described in [8]. The structure of MCM-22 contains two independent channel systems, 10-MR sinusoidal channels and 12-MR cages linked by 10-MR channels. The topology of MCM-22 is more open than that of ZSM-5. The same procedure used for Mo/HZSM-5 was applied to prepare the catalyst Mo/H-MCM-22 with 4 wt.% Mo. 4 wt.% Mo/SiO<sub>2</sub> was also prepared by incipient wetness impregnation of SiO<sub>2</sub> (W.G. Grace, surface area = 250 m<sup>2</sup>/g).

### 2.2. Reaction

Methane reaction was performed in a flow microreactor at atmospheric pressure on 300 mg of the catalyst. Non-diluted CH<sub>4</sub> at atmospheric pressure flows through the catalyst bed, WHSV was in the range

1.2–0.7 h<sup>-1</sup>. The reaction temperature was 923 K. CH<sub>4</sub> and H<sub>2</sub> were analyzed with a catharometer chromatograph equipped with a silica gel column. The products, ethylene, benzene, naphthalene, toluene, were analyzed on flame ionization chromatograph equipped with a bentone and an unibed column.

CH<sub>4</sub> conversion is low and could not be determined with accuracy from CH<sub>4</sub> peak. Therefore CH<sub>4</sub> which has reacted was calculated from the measured H<sub>2</sub> pressure and from the sum of hydrogen contained in the hydrocarbons. It is implied that carbon species (coke) which may have deposited on the catalyst surface was free from hydrogen. The amount of coke deposited on the surface was derived from the difference between carbon corresponding to reacted CH<sub>4</sub> and carbon corresponding to the hydrocarbons formed.

## 3. Results and discussion

When CH<sub>4</sub> was reacted at 923 K on the oxidized Mo/HZSM-5 sample large amount of H<sub>2</sub> evolved at the initial stage of the reaction. During this period almost no hydrocarbon was formed. Fig. 1 represents the conversion of methane, derived from H<sub>2</sub> and hydrocarbons, with time on stream (TOS). The selectivities of the reaction to coke, benzene, naphthalene and ethylene are given in Fig. 2. Analysis of these two figures clearly indicates that at the early stage of the reaction while a significant amount of CH<sub>4</sub> has reacted, negligible amounts of benzene, naphthalene and ethylene were observed.

The major products were H<sub>2</sub> and coke in agreement with previous published works [3,4]. During the initial period of the reaction, 0.5–1 h, the selectivity for benzene, naphthalene, ethylene increased until a plateau was reached, see Fig. 2. With increasing TOS CH<sub>4</sub> conversion decreased gradually and simultaneously the selectivity for coke. From these results it is concluded in agreement with the statements made in [4] that during the induction period MoO<sub>3</sub> or/and (MoO<sub>2</sub>)<sup>n+</sup> suboxides supported on the zeolite react with CH<sub>4</sub> to form molybdenum carbide species and H<sub>2</sub>. It has already been established that supported molybdenum reacts with methane to form Mo<sub>2</sub>C [9]. XPS results have confirmed the formation of Mo<sub>2</sub>C upon reaction of CH<sub>4</sub> with Mo/HZSM-5 at high temperature [4]. The formation C–C bond, first step of

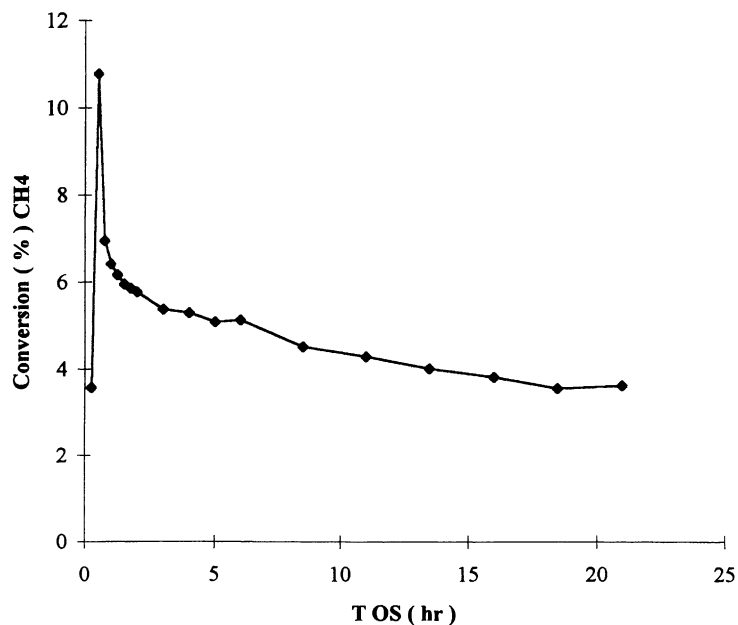


Fig. 1. Conversion of CH<sub>4</sub> at 923 K, WHSV = 0.7 h<sup>-1</sup>, atmospheric pressure with TOS on Mo/HZSM-5.

the formation of C<sub>2</sub> hydrocarbons and aromatics is probably associated with the generation of Mo<sub>2</sub>C species. One could suggest that on Mo<sub>2</sub>C active sites, the decomposition of CH<sub>4</sub> resulted in the formation of carbidic surface carbon more or less hydrogenated.

At high temperatures, as used in the aromatization, surface coverage by hydrogen is low, CH<sub>2</sub> and preferably CH hydrogenated carbidic fragments are present. C–C bonds will be formed upon surface migration of the partially hydrogenated carbidic carbons.

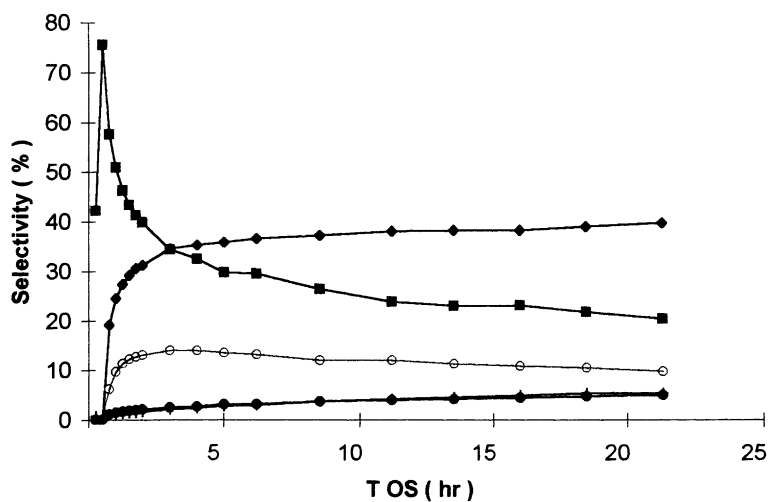


Fig. 2. Reaction of CH<sub>4</sub> on Mo/HZSM-5 at 923 K, WHSV = 0.7 h<sup>-1</sup>. Product selectivity with TOS: (■) coke; (◆) benzene; (○) naphthalene; (●) ethylene.

Na-ZSM-5 (Si/Al = 26) was obtained by reexchange of H-ZSM-5 with Na<sup>+</sup> solution. The solid was then loaded with 4 wt.% Mo. The rate of benzene formation over the catalyst Mo/Na ZSM-5 was less than one-tenth of that found on Mo/HZSM-5. It was suggested that the aromatization of methane obeyed a bifunctional mechanism, ethylene formed on the Mo sites will form benzene through carbenium ion mechanism catalyzed by the zeolite protons [1,3,6]. More recently the bifunctional mechanism for the aromatization of methane has again been suggested [10]. The authors have observed that the rate of benzene formation from the reaction of CH<sub>4</sub> on Mo/HZSM-5 catalysts decreased as the Si/Al increased (the support acidity decreasing as Si/Al increased). They also proposed that methane activated on Mo<sub>2</sub>C formed C<sub>2</sub>H<sub>4</sub>, ethylene being converted into benzene on the ZSM-5 acid sites. The rates of benzene formation from the reaction of CH<sub>4</sub> on a series of Mo/H-ZSM-5 where the Si/Al ratio increased are given in Table 1.

The results listed in Table 1, showing a strong dependence of the rate of benzene formation on Si/Al ratio are in agreement with previous works [1,3,6].

Table 1

Reaction of CH<sub>4</sub> on Mo/HZSM-5: effect of Si/Al ratio on the rate (*R*) of benzene production (*T<sub>R</sub>* = 923 K, WHSV = 0.7 h<sup>-1</sup>, CH<sub>4</sub> atmospheric pressure)

Si/Al	15	26	50	130
Mo (wt.%)	4	4	4	4
<i>R</i> (μmol g <sup>-1</sup> h <sup>-1</sup> )	168	125	80	48

However, we could suggest a different interpretation for this effect. Indeed, during the activation of Mo/HZSM-5, Mo species migrated within the zeolite lattice and exchanged with H<sup>+</sup> [4–6]. We suggest that, since higher the Si/Al ratio, lesser the number of exchangeable H<sup>+</sup>, the increase of Si/Al renders less probable the stabilization of atomically dispersed Mo species. In other words, the dispersion of the active Mo species will decrease as Si/Al increases. CH<sub>4</sub> being activated on these Mo species the aromatization activity will decrease. This point will be discussed further.

The catalytic performances of Mo/HZSM-5 (Si/Al = 15) and Mo/HMCM-22 (Si/Al = 15) were compared. Fig. 3 shows the rate of benzene formation from CH<sub>4</sub> at 923 K. After the induction period, the

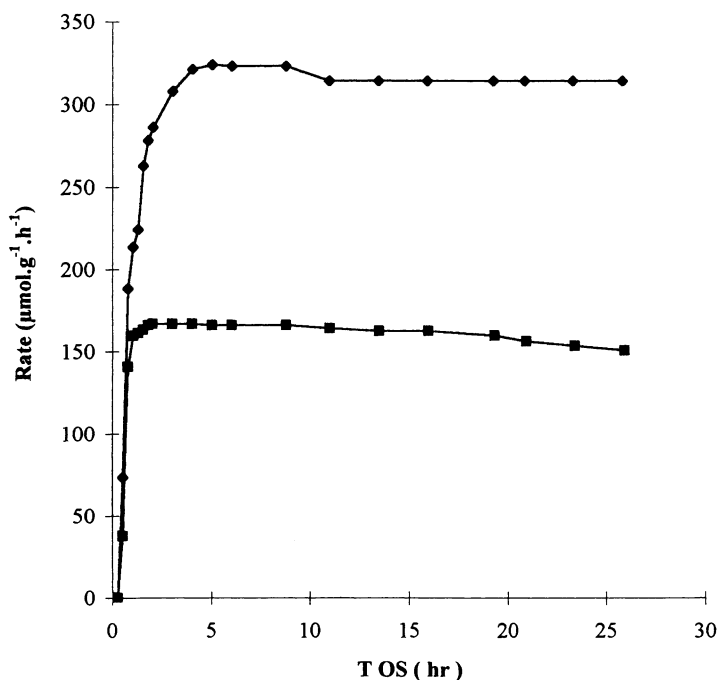


Fig. 3. Reaction of CH<sub>4</sub> on zeolite supported Mo (Si/Al = 15): rate of benzene formation at 923 K, WHSV = 0.7 h<sup>-1</sup>. (■) Mo/HZSM-5; (◆) Mo/HMCM-22.

rates reached a semi plateau. The rates for benzene production are 168 and 328  $\mu\text{mol g}^{-1} \text{h}^{-1}$  and the selectivity towards benzene are 40 and 80%, respectively for Mo/HZSM-5 and Mo/HMCM-22. It appears that the use of HMCM-22 as support for molybdenum resulted in catalyst more active and more selective for the conversion of methane into benzene as compared with Mo/HZSM-5. The higher selectivity to benzene with Mo/HMCM-22 was due to less coke deposition on the catalyst. After 20 h on stream, on Mo/HMCM-22,  $\text{CH}_4$  at 923 K was almost exclusively converted into benzene (80%) naphthalene (10%) and coke (10%). Apparently, H-MCM-22 is a more appropriate support for the aromatization of methane on Mo based catalysts. At 923 K with  $\text{WHSV} = 0.7 \text{ h}^{-1}$  the yield of aromatics (benzene + naphthalene) was respectively 1.5 and 3.8% for Mo/HZSM-5 and Mo/HMCM-22 (thermodynamic 4.6%). Two factors govern the efficiency of the molybdenum based catalysts, the dispersion of Mo species and the diffusion of the bulky aromatic molecules produced within the zeolite pores.

Within Mo/HMCM-22, in the 12-MR surface half cavities, the diffusion of benzene and naphthalene

is less constrained than in ZSM-5 pores. Similarly, the coke precursor aromatic intermediates could also escape more readily. The better efficiency of Mo/HMCM-22 is thus attributed to its more open topology allowing a better dispersion of the molybdenum species and a more rapid diffusion of the reaction products.

### 3.1. Role of the zeolite in the aromatization of methane

In the previous section it was suggested that the role of the zeolite is to provide cation exchange sites where cationic molybdenum species atomically dispersed were stabilized. The migration of Mo species was indirectly studied by infrared (IR) spectroscopy. H-MCM-22 sample showed in the OH stretching vibration two IR bands at  $3750 \text{ cm}^{-1}$  attributed to terminal Si-OH non-acidic groups and at  $3622 \text{ cm}^{-1}$  due to bridge Si-OH (Al) acidic groups. The intensity of this IR band is increasing when the Al content increases. The effects of impregnation, calcination in oxygen at 873 K and reaction with  $\text{CH}_4$  at 923 K are

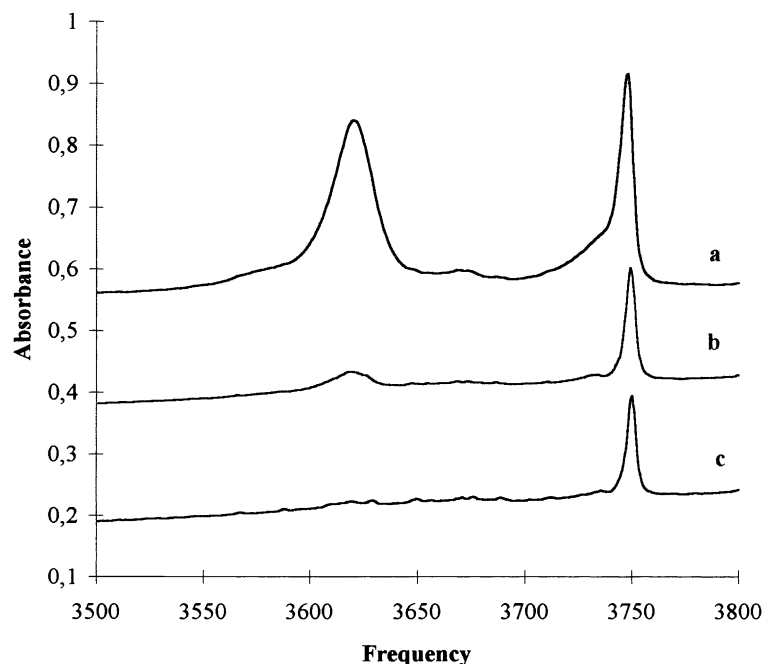


Fig. 4. IR spectra in the OH region: (a) 4 wt.% Mo/HMCM-22 impregnated with Mo; (b) sample a calcined in  $\text{O}_2$  at 873 K; (c) sample b after activation at 923 K in  $\text{CH}_4$ .

shown in Fig. 4. The impregnation of the solid with Mo heptamolybdate has little effect on the exchangeable OH groups as long as the calcination temperature is less than 473 K. At 873 K in oxygen, molybdenum suboxides  $(\text{MoO}_2)^+$  and  $(\text{Mo}_2\text{O}_5)^{2+}$ , migrated in the zeolite framework and exchanged with  $\text{H}^+$ . It resulted a strong decrease of the  $3622\text{ cm}^{-1}$  IR band intensity as shown in Fig. 4. Further reaction with  $\text{CH}_4$  at 923 K resulted to an additional decrease of the  $3622\text{ cm}^{-1}$  IR band intensity, due probably to the deposition of carbonaceous residues. From these results, it is concluded that indeed the cationic sites of the zeolite serve as site anchors for molybdenum which forms upon reaction with  $\text{CH}_4$  highly dispersed molybdenum carbide. The very high mobility of suboxide molybdenum species and the anchoring on cationic sites was reinforced by the following experiments. 4 wt.%  $\text{MoO}_3/\text{SiO}_2$  was mechanically mixed with equal amount of H-ZSM-5. H-ZSM-5 +  $\text{Mo}/\text{SiO}_2$  composite solid was outgassed at 473 K and its IR spectrum recorded. IR bands at  $3750$  and  $3622\text{ cm}^{-1}$  were observed. Upon calcination at 873 K in oxygen, non-IR band at  $3622\text{ cm}^{-1}$  existed. This indicates that Mo suboxide species had migrated from the  $\text{SiO}_2$  surface to the zeolite and have exchanged with  $\text{H}^+$  of the zeolite. The reaction of  $\text{CH}_4$  at 923 K over H-ZSM-5,  $\text{Mo}/\text{SiO}_2$  and H-ZSM-5 +  $\text{Mo}/\text{SiO}_2$  composite was studied. The conversion and the rate of benzene formation are given in Table 2.

The higher activity of the composite catalyst is due to the increase of the Mo dispersion in the composite solid, this increase being caused by the migration of Mo into the zeolite framework where it was stabilized and atomically dispersed. Since the IR results on  $\text{Mo}/\text{HMCM-22}$  and on  $\text{Mo}/\text{SiO}_2 + \text{HMCM-22}$  have shown that protonic acidity on these two catalysts has almost disappeared, it is difficult to consider that the aromatization of methane proceeds through a bifunctional reaction.

Table 2

Reaction of  $\text{CH}_4$  on Mo catalysts ( $T_R = 923\text{ K}$ ,  $\text{WHSV} = 0.7\text{ h}^{-1}$ , rate of benzene formation ( $R$ ))

Catalyst	H-ZSM-5	$\text{Mo}/\text{SiO}_2$	$\text{Mo}/\text{SiO}_2 + \text{HZSM-5}$
Conversion (%)	0.7	1.2	3.5
$R$ (benzene) ( $\mu\text{mol g}^{-1}\text{ h}^{-1}$ )	0	40	94

### 3.2. Reaction intermediate—reaction mechanism for the aromatization of methane on $\text{Mo}/\text{HZSM-5}$

It is generally suggested that the most likely intermediate from the reaction of  $\text{CH}_4$  on supported molybdenum is  $\text{C}_2\text{H}_4$  [1–6].  $\text{C}_2\text{H}_4$  could result via a carbene-type intermediate or via carbidic surface species, the methane being dehydrogenated over  $\text{Mo}_2\text{C}$ . It was suggested that the formed ethylene undergoes oligomerization and cyclization reactions catalyzed on acid sites of the zeolite. The reaction of methane over  $\text{Mo}/\text{HZSM-5}$  has been reinvestigated using GC-MS to analyze the products.  $\text{CH}_4$  reaction was carried out at 1023 K at different flow rates. In addition to ethylene, benzene and naphthalene, acetylene was for the first time detected in the reaction products [7]. Fig. 5 shows the relative pressures of  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$  and benzene versus the flow rate. The interesting point is that the acetylene pressure

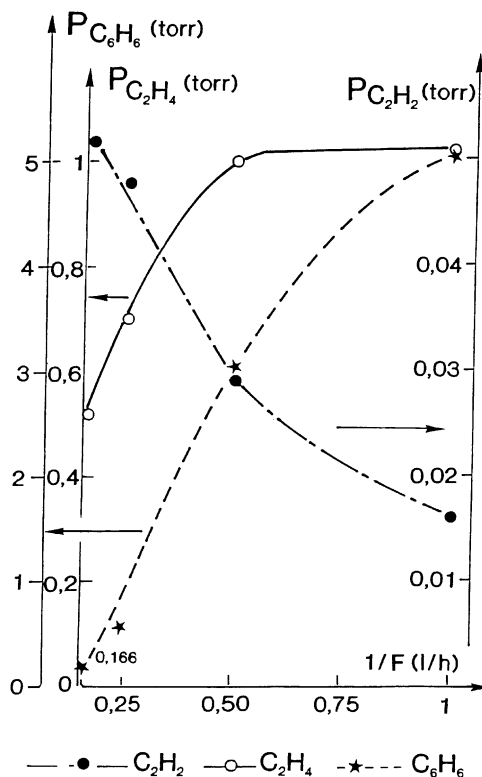


Fig. 5. Reaction of  $\text{CH}_4$  over  $\text{Mo}/\text{HZSM-5}$  at 1023 K. Product distribution versus flow rate.

Table 3  
Rate of C<sub>6</sub>H<sub>6</sub> formation from CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub> (*T<sub>R</sub>* = 923 K, WHSV = 0.07 h<sup>-1</sup>, *R* (μmol g<sup>-1</sup> h<sup>-1</sup>))

Catalyst/feed	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>2</sub>
H-ZSM-5	0	25	193
Mo/SiO <sub>2</sub>	47	50	68
Mo/HZSM-5	131	97	144

increases as the contact time decreases, the reverse being observed for ethylene and benzene. These results suggest that C<sub>2</sub>H<sub>2</sub> acts probably as the primary product for benzene formation. It is well accepted that acetylene readily forms benzene at high temperature this reaction being catalyzed by metals.

The effect of proton acid sites and Mo<sub>2</sub>C sites on the formation of benzene was further studied by using HZSM-5, Mo/SiO<sub>2</sub> and Mo/HZSM-5 catalysts for the reaction of CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub>. The catalysts were activated in oxygen and in CH<sub>4</sub> at 923 K until the steady state was reached. The catalysts were purged with H<sub>2</sub> and then either C<sub>2</sub>H<sub>4</sub>/H<sub>2</sub>/N<sub>2</sub> or C<sub>2</sub>H<sub>2</sub>/H<sub>2</sub>/N<sub>2</sub> mixture (6/30/724 Torr) was allowed on these solids. Table 3 lists the rates of benzene production.

Not surprisingly methane, ethylene, and acetylene showed different reactivity. Over non-promoted H-ZSM-5 the conversion of methane was very low and almost negligible amount of benzene was formed. The interesting point was that benzene was formed eight times more rapidly with acetylene feed than with ethylene. These results reinforce our suggestions that over Mo/HZSM-5, C<sub>2</sub>H<sub>2</sub> formed from the reaction of CH<sub>4</sub> will be the main source of aromatics if some residual protons participate to the aromatization reaction. It has been shown that the conversion of acetylene to aromatics proceeds more easily than that of ethylene over H-ZSM-5 catalyst [11]. The reaction intermediate responsible for the oligomerization and cyclization is of considerably greater reactivity from acetylene than that involved in ethylene conversion. The oligomerization of acetylene proceeds via vinyl cation intermediate CH<sub>2</sub>=CH<sup>+</sup> while the chain growth from the ethylene involves less reactive primary ethylcarbenium intermediate CH<sub>3</sub>-CH<sub>2</sub><sup>+</sup> in Bronsted acid catalyzed reactions. The formation of hexadiene cation CH<sub>2</sub>=CH-CH=CH-CH=CH<sup>+</sup> from acetylene favors the production of benzene via its ther-

modynamic favorable cyclization at high temperature. Over Mo/SiO<sub>2</sub> catalyst which does not possess proton acidity the rate of benzene formation does not change much with the feed (see Table 3) although C<sub>2</sub>H<sub>2</sub> was again the most reactive. The reactions occurring involves the formation of acetylene obviously on molybdenum carbide (Mo<sub>2</sub>C) dehydrogenating sites. The polymerization of acetylene to polyenes and hexadiene, most certainly involves reaction at Mo<sub>2</sub>C. Acetylene polymerization to polyenes is well known using Ziegler-Natta catalysts [12] and certain types of Lewis acid solids [13]. Over Mo/HZSM-5 the relative rates of benzene formation were higher than those measured on Mo/SiO<sub>2</sub> catalyst. The increased efficiency of Mo/HZSM-5 support compared to Mo/SiO<sub>2</sub> is ascribed to HZSM-5 support which increases the dispersion of molybdenum species. At the same molybdenum content Mo<sub>2</sub>C exposed surface will be higher on HZSM-5. The conversion of CH<sub>4</sub> over Mo/HZSM-5 will be higher on Mo/SiO<sub>2</sub> in agreement with our results. The use of acid support HZSM-5 for Mo<sub>2</sub>C instead of SiO<sub>2</sub> renders the aromatization of C<sub>2</sub>H<sub>4</sub> as well as C<sub>2</sub>H<sub>2</sub> faster. Although in this section we have pointed out that the activation treatments at high temperature in oxygen and in methane removed and/or poisoned almost all the protonic acid sites of the zeolite the observed the increase of benzene rate over Mo/HZSM-5 implies that very few H<sup>+</sup> may be enough to catalyze the formation of polyenes from acetylene.

#### 4. Conclusion

Mo loaded medium pore zeolites are active and selective for the conversion of methane to aromatics. At reaction temperature higher than 923 K the major product is benzene followed by naphthalene on 4 wt.% Mo loaded zeolites. The yields of aromatics formed on Mo/HZSM-5 and Mo/HMCM-22 were, respectively, 2 and 3.4% at 923 K. The higher efficiency of HMCM-22 support corresponds to a better dispersion of molybdenum and to a faster diffusion of molecules. The initial product of the methane reaction is acetylene and possibly ethylene. They are formed by dehydrogenation of CH<sub>4</sub> on molybdenum carbide Mo<sub>2</sub>C. Mo<sub>2</sub>C being generated from the reaction of MoO<sub>3</sub> or other Mo suboxides with CH<sub>4</sub>. The

activity of the composite catalysts Mo/support is considerably dependent on the dispersion of Mo<sub>2</sub>C, the highest dispersion producing the most active solid. The reaction mechanism for the production of aromatics proceeds either via a monofunctional mechanism where acetylene, the primary product, is oligomerized on Mo<sub>2</sub>C into polyene such as hexadiene and cyclized thermally into aromatics, or/and acetylene (ethylene to a less extent) is forming higher-molecular weight polyenes via a vinyl cation intermediate on Bronsted acid sites. This latter reaction is extremely fast and requires a limited number of protonic sites.

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