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Methane aromatization over Mo/H-ZSM-5: on the reaction pathway

P. Mériaudeau, Vu Thi Thu Ha and Le Van Tiep
IRC/CNRS, 2, avenue A. Einstein, 69626 Villeurbanne, France
E-mail: meriaud@catalyse.univ-lyon1.fr

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Rates of benzene formation on Mo/HZSM-5, H-ZSM-5 and Mo/SiO_2 were measured with different reactants: methane, mixture of $C_2H_4/H_2/N_2$ and mixture of $C_2H_2/H_2/N_2$. Since the rate of benzene formation starting from $C_2H_4/H_2/N_2$ is higher on Mo/H-ZSM-5 compared to H-ZSM-5 it is concluded that the aromatization of methane on Mo/H-ZSM-5 is not going via ethylene which is aromatized over acid sites. Another reaction pathway is proposed.

Keywords: methane aromatization, ethylene aromatization, acetylene aromatization

1. Introduction

The aromatization of methane has been deeply investigated since Xu et al. [1,2] have reported that molybdenum-loaded H-ZSM-5 are active catalysts for this reaction at high temperatures (600–800 °C).

Lunsford et al. [3] have shown that under thermal treatment at high temperatures under air or oxygen, the molybdenum salt is decomposed and Mo ions migrated in the zeolite channels and are exchanged with the protons of the zeolite.

The migration of molybdenum has been confirmed recently by Iglesia et al. [4], who have shown that every proton removed from an exchangeable position is replaced by one Mo ion.

It results that the high-temperature calcined catalyst has less protons than the starting material.

Lunsford et al. [3] have also shown that under methane molybdenum is transformed into Mo_2C which was idendified as the active phase for methane activation.

However, the exact nature of the active phase – coke modified Mo_2C [3] or Mo_2C–MoO_2 [5] – is still matter of discussions. As indicated above, it is nevertheless well established that the catalyst in its active state contains only a small number of protons as compared to the number of protons of the starting H-ZSM-5 [3].

The mechanism of the reaction has been debated: it is generally proposed that methane is activated over molybdenum carbide species where it forms ethylene as the primary product.

Ethylene is then converted into benzene over the zeolite support through acid-catalyzed oligomerization and cyclization reactions [2–6]. Thus the zeolite-supported molybdenum catalysts operate like a true bifunctional catalyst.

However, recently, we have shown that the reaction of methane over Mo/H-ZSM-5 resulted in the production of acetylene which was considered as the primary product and that the formation of benzene did not proceed necessarily through acid type reaction [7].

The aim of this note is to further demonstrate that over Mo/H-ZSM-5 catalyst, it is highly questionable that benzene was formed through the aromatization of ethylene over protonic sites following the classical acid reaction mechanisms.

2. Materials and results

H-ZSM-5 zeolite (Si/Al = 26, batch 1381 from Sud Chemie, Germany) was loaded with 4 wt% Mo (wetness impregnation with ammonium heptamolybdate from Aldrich). The sample was dried at 120 °C overnight.

300 mg of the sample were loaded in a microflow reactor and treated under air overnight at 650 °C. Reactant and products were analyzed on line with two chromatographs equipped with a Bentone column (for the analysis of aromatics) and with a Unibed column (for the analysis of light hydrocarbons).

For comparison, H-ZSM-5 support and 4 wt% Mo/SiO_2 (Degussa, wetness impregnated) were studied in the same experimental conditions.

Three sets of reaction were carried over the same sample loaded in the reactor:

(i) CH_4 was reacted with the air-activated sample and the rate of formation of benzene measured with time on stream. When the rate has reached a pseudo steady state, the reactor was flushed with N_2 for 20 min.

(ii) A mixture of $C_2H_4/H_2/N_2$ (partial pressures 6/30/724 Torr) was then reacted over the previous sample. The rate of benzene formation with time on stream was determined – when the steady state was reached, the reactor was again flushed with nitrogen for 20 min.

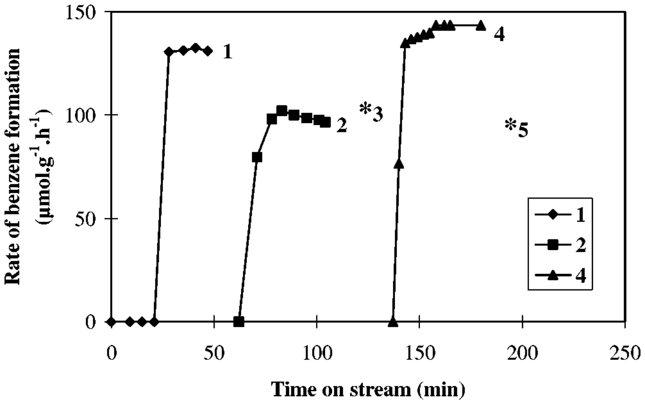

Figure 1. Change in the rate of benzene formation on 4 wt% Mo/H-ZSM-5 with time on stream for different reactants: (1) CH_4, atmospheric pressure; (2) $C_2H_4 + H_2 + N_2$ (6/30/724 Torr); (*3) CH_4, atmospheric pressure; (4) $C_2H_2+H_2+N_2$ (6/30/724 Torr); and (*5) CH_4, atmospheric pressure. $T = 650\,^\circ$C, catalyst weight 300 mg, total flow rate 2 l/h.

(iii) Methane was again reacted as in (i) and the rate of benzene formation measured and the reactor was again flushed with nitrogen for 20 min.

(iv) A mixture of $C_2H_2/H_2/N_2$ (partial pressures 6/30/724 Torr) was reacted over the catalyst and the formation of benzene followed until the steady state was reached. Again the reactor was flushed with nitrogen for 20 min.

(v) Methane was again reacted, as in (i) and (iii).

The experimental points obtained in (iii) and (v), compared to (i), indicated the extent of deactivation of the catalyst.

Results are summarized in figure 1 for 4 wt% Mo/H-ZSM-5, figure 2 for H-ZSM-5 and figure 3 for 4 wt%/SiO_2.

For 4 wt% Mo/H-ZSM-5, the maximum rate for benzene formation from methane was 131 μmol h^{-1} g^{-1} at 50 min.

When C_1 was replaced by the ethylene-containing mixture the maximum rate for benzene formation was 100 μmol h^{-1} g^{-1}.

At this stage, the catalyst was slightly deactivated since the rate of benzene formation starting from methane was equal to 110 μmol h^{-1} g^{-1} (see *3 in figure).

The rate of benzene formation starting from acetylene mixture is at the steady state equal to 144 mol h^{-1} g^{-1}. Again the last experimental point indicated that the catalyst has lost part of its activity since the rate measured (using methane) is now 100 mol h^{-1} g^{-1} (point *5 in figure 1).

These results indicated that the Mo/H-ZSM-5 catalyst deactivated during the reactions but not too much. The fact that the different reactants produced benzene with comparable rates indicated that ethylene as postulated by [1–6] or acetylene as postulated by us [7] are possible intermediates.

Comparison between Mo/H-ZSM-5 and H-ZSM-5 is interesting and indicated that the rate of benzene formation starting from the $C_2H_4/H_2/N_2$ mixture is much smaller on the support H-ZSM-5 than on Mo/H-ZSM-5 (25 μmol h^{-1} g^{-1} compared to 100 μmol h^{-1} g^{-1}).

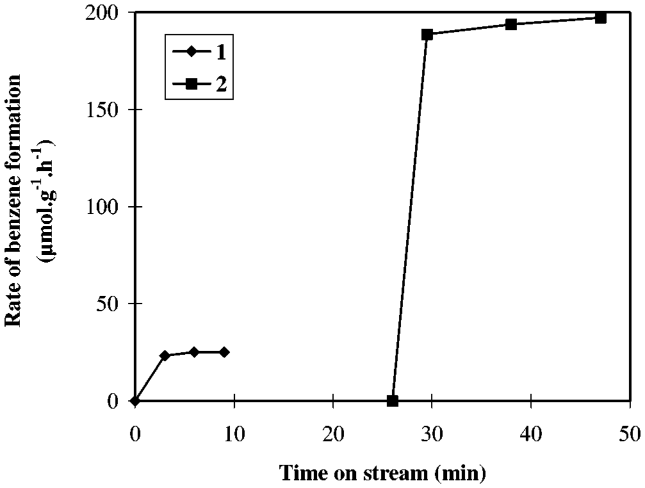

Figure 2. Change in the rate of benzene formation on H-ZSM-5 with time on stream with different reactants: (1) $C_2H_4/H_2/N_2$ (6/30/724 Torr) and (2) $C_2H_2/H_2/N_2$ (6/30/724 Torr). $T = 650\,^\circ$C, catalyst weight 300 mg, total flow rate 2 l/h.

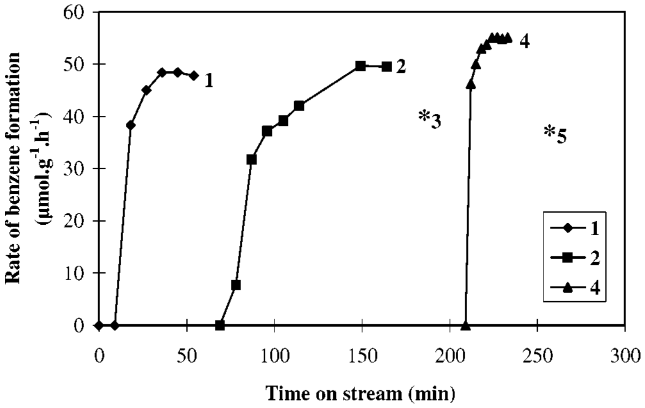

Figure 3. Change in the rate of benzene formation over 4 wt% Mo/SiO_2: (1) CH_4, atmospheric pressure; (2) $C_2H_4/H_2/N_2$ (6/30/724 Torr); (*3) CH_4, atmospheric pressure; (4) $C_2H_4/H_2/N_2$ (6/30/724 Torr); and (*5) CH_4, atmospheric pressure. $T = 650\,^\circ$C, catalyst weight 500 mg, total flow rate 2 l/h.

Knowing that the number of remaining protons on Mo/H-ZSM-5 is smaller than on the support ([3,4] and our unpublished results) it can be concluded that if C_2H_4 is the true intermediate, it is not, as proposed in the literature, aromatized through a pure acid type reaction.

Comparison between Mo/H-ZSM-5 and Mo/SiO_2 indicates that, as reported in the literature, SiO_2 support is much less efficient than H-ZSM-5 for methane aromatization. Interestingly, it is observed that Mo/SiO_2 is much more active than H-ZSM-5 for benzene formation when the feed is $C_2H_4/H_2/N_2$.

This result indicates that Mo species (carbidic or oxycarbidic Mo?) could be the active species for aromatization of ethylene or that they are involved in the ethylene aromatization. Results of figures 1 and 3 indicated that Mo/H-ZSM-5 is twice more active than Mo/SiO_2 for ethylene aromatization; this could be due to a better dispersion of Mo species over H-ZSM-5 support.

Indeed, one can postulate that Mo_2C/SiO_2 could have protons and thus C_2H_4 aromatization could occur via a bifunctional mechanism (oligomerization, cyclization over protonic sites, hydrogen removal over Mo_2C).

The important point is that the presence of protons is not the only condition for ethylene aromatization as it was indicated [4].

Concerning the transformation of acetylene into benzene, it is observed that the three solids (Mo/HZSM-5, HZSM-5 and Mo/SiO_2) are active, the zeolite-based catalysts having the highest activity.

Should acetylene be the intermediate, its transformation into benzene would not be restricted by the number of protons.

To summarize, we have shown that the reaction mechanism of methane aromatization is not as simple as described in the literature: the key intermediates are probably acetylene or ethylene.

Should ethylene be the intermediate its transformation into benzene would not occur as proposed on the protons of the zeolite, but molybdenum entities would catalyze its aromatization.

References

[1] L. Wang, L. Tao, M. Xie, G. Xu, J. Huang and Y. Xu, Catal. Lett. 21 (1993) 35.

[2] Y. Shu, Y. Xu, S.T. Wong, L. Wang and X. Guo, J. Catal. 170 (1997) 11.

[3] D. Wang, J.H. Lunsford and M.P. Rosynek, J. Catal. 169 (1997) 347.

[4] R.W. Borry III, E.C. Lu, Y. Ho Kim and E. Iglesia, in: *Stud. Surf. Sci. Catal.*, Vol. 119 (Elsevier, Amsterdam, 1998) p. 403.

[5] F. Solymosi, A. Erdöhelyi and A. Szöke, Catal. Lett. 32 (1995) 43.

[6] S. Lice, L. Wang, R. Onishi and M. Ichikawa, J. Catal. 181 (1999) 175.

[7] P. Mériaudeau, V.T.T. Ha, L.V. Tiep and G. Szabo, J. Mol. Catal. (1999), in press.