EUROPACAT – VII

«CATALYSIS: A KEY TO REACHER AND CLEANER SOCIETY»

Methane dehydroaromatization on Mo/ZSM-5 catalysts: structure of active sites and carbonaceous deposits during catalytic cycle

E.V. Matus[1], Z.R. Ismagilov[1], V.I. Zaikovskii[1], L.T. Tsikoza[1], N.T. Vasenin[1], O.B. Sukhova[1], I.Z. Ismagilov[1,2], M.A. Kerzhentsev[1], V. Keller[2], N. Keller[2], F. Garin[2]

[1] Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
[2] LMSPC, Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse, Strasbourg, France

28 August – 1 September, 2005, Sofia Bulgaria

Methane dehydroaromatization (DHA) over Mo/ZSM-5 catalysts - a new perspective environmentally-friendly way to obtain both valuable aromatics and hydrogen

$$6CH_4 \Rightarrow C_6H_6 + 9H_2$$

bifunctional catalyst

$$MoO_x \overset{CH_4}{\Longrightarrow} Mo_2C \text{ (or } MoO_yC_z)$$

$2CH_4 \Rightarrow C_2H_6 \Rightarrow C_2H_4$ on formed Mo_2C (or MoO_yC_z),

$3C_2H_4 \Rightarrow C_6H_6$, etc. on HZSM-5

equilibrium CH_4 conversion to benzene under non-oxidative conditions at 720°C is about 12%.

Methane dehydroaromatization (DHA) over Mo/ZSM-5 catalysts: main questions

- What is the nanostructure and localization of the active molybdenum species ?

- What is the nature of unwanted carbonaceous deposits formed during the reaction and how to minimize their formation ?

- Reaction mechanism

- How to make the DHA of methane a commercially applicable process ?

Approach - systematic study of the state of Mo at all stages of Mo/ZSM-5 preparation and catalytic cycle:

catalyst preparation:

- selection of molybdenum precursor
- preparation of impregnation solutions
- catalyst after treatment in air at 110ºC, 500ºC and 700ºC

catalytic cycle:

- catalyst after pretreatment in Ar at 720ºC
- catalyst after the CH_4 DHA reaction at 720ºC
- past reaction catalyst after treatment in O_2 at 600ºC

depending on Si/Al ratio in the parent H-ZSM-5 and on Mo content

Preparation of Mo/ZSM-5 catalysts

Method of incipient wetness impregnation of zeolite H-ZSM-5 by solution of ammonium heptamolybdate (**$(NH_4)_6Mo_7O_{24}$*$4H_2O$, AHM)** at controlled value of solution pH

VARIATION of CONDITIONS

⇓ ⇓

<u>impregnation</u>

- concentration of AHM solution
- pH of AHM solution
- Si/Al atomic ratio of H-ZSM-5 zeolite

<u>thermal treatment</u>

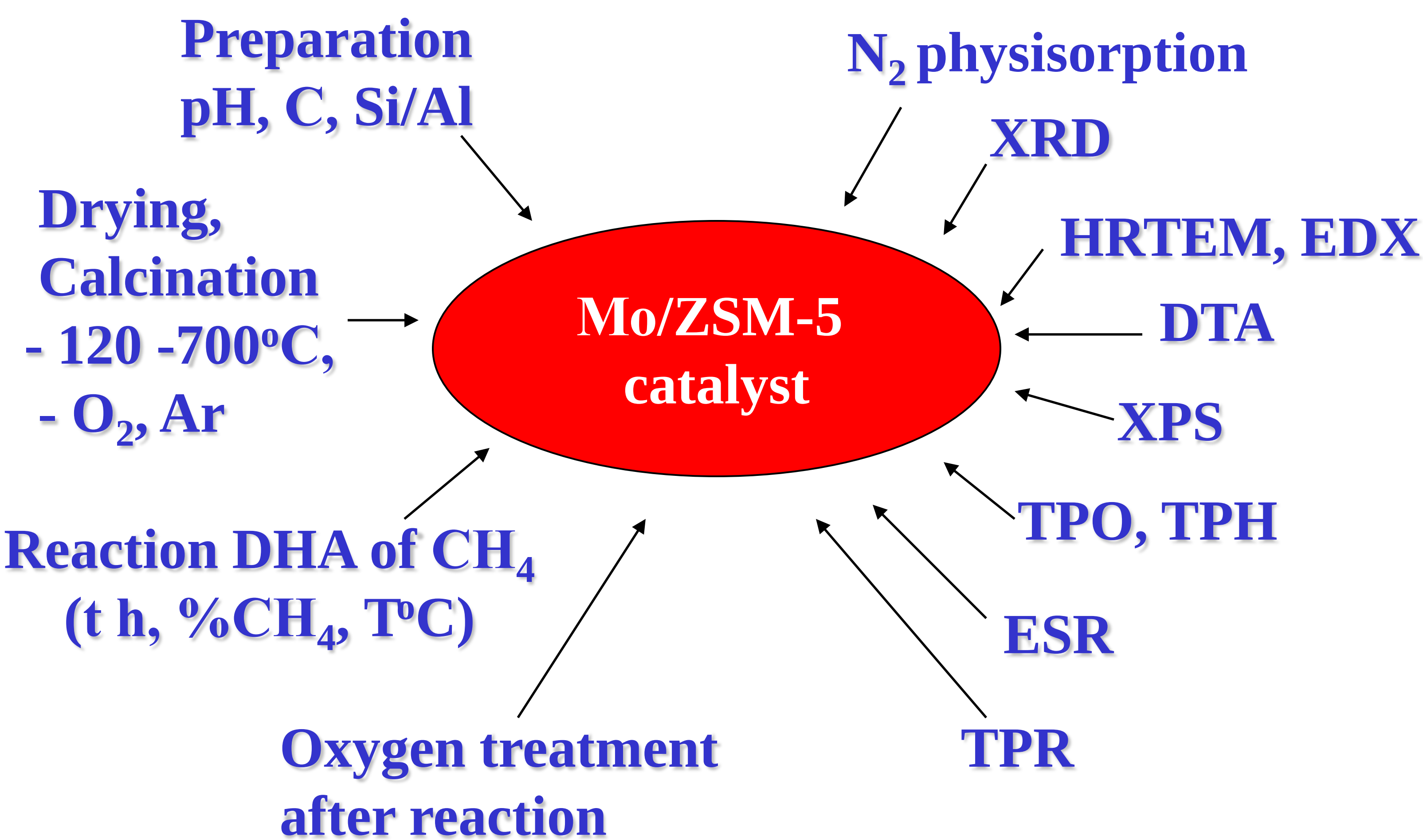
- temperature
- composition of medium (air, Ar)

⇓

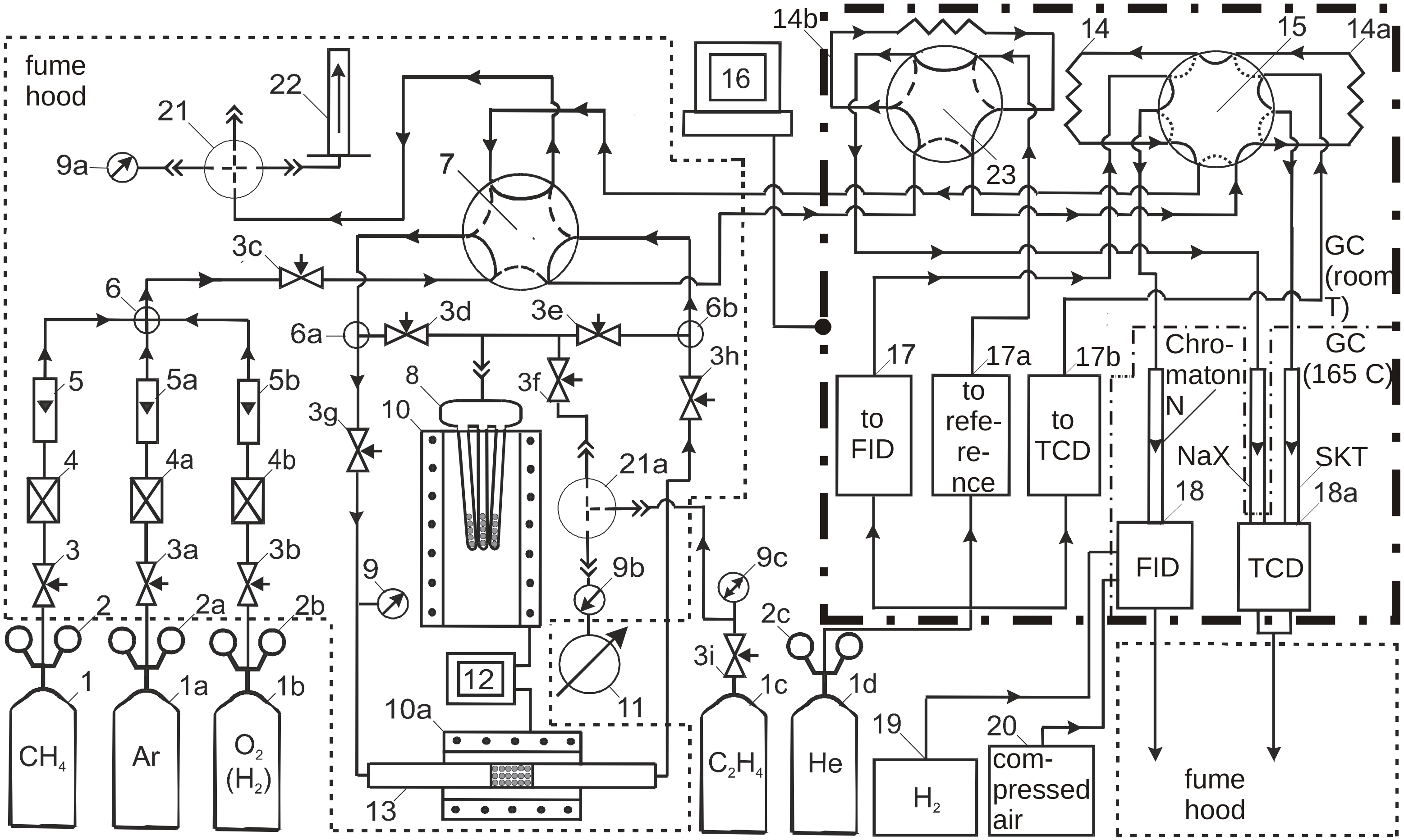
?

PHYSICO-CHEMICAL PROPERTIES and ACTIVITY of Mo/ZSM-5 CATALYSTS

Investigation of Mo/ZSM-5 catalysts by group of methods

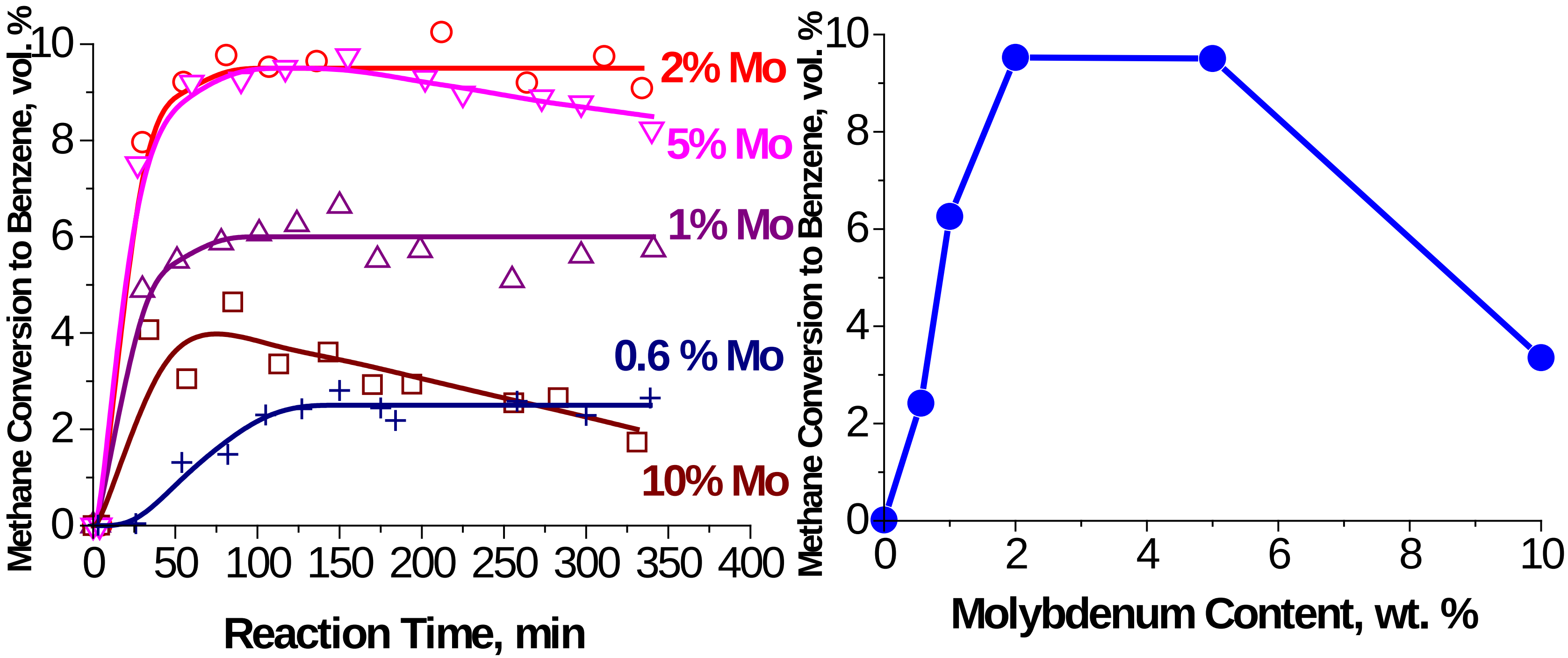


Laboratory flow setup for CH_4 DHA



Test conditions: load = 1.0 cm^3 (0.6 g); fraction = 0.25-0.5 mm
flow = 13.5 cm^3/min; GHSV = 810 h^{-1}

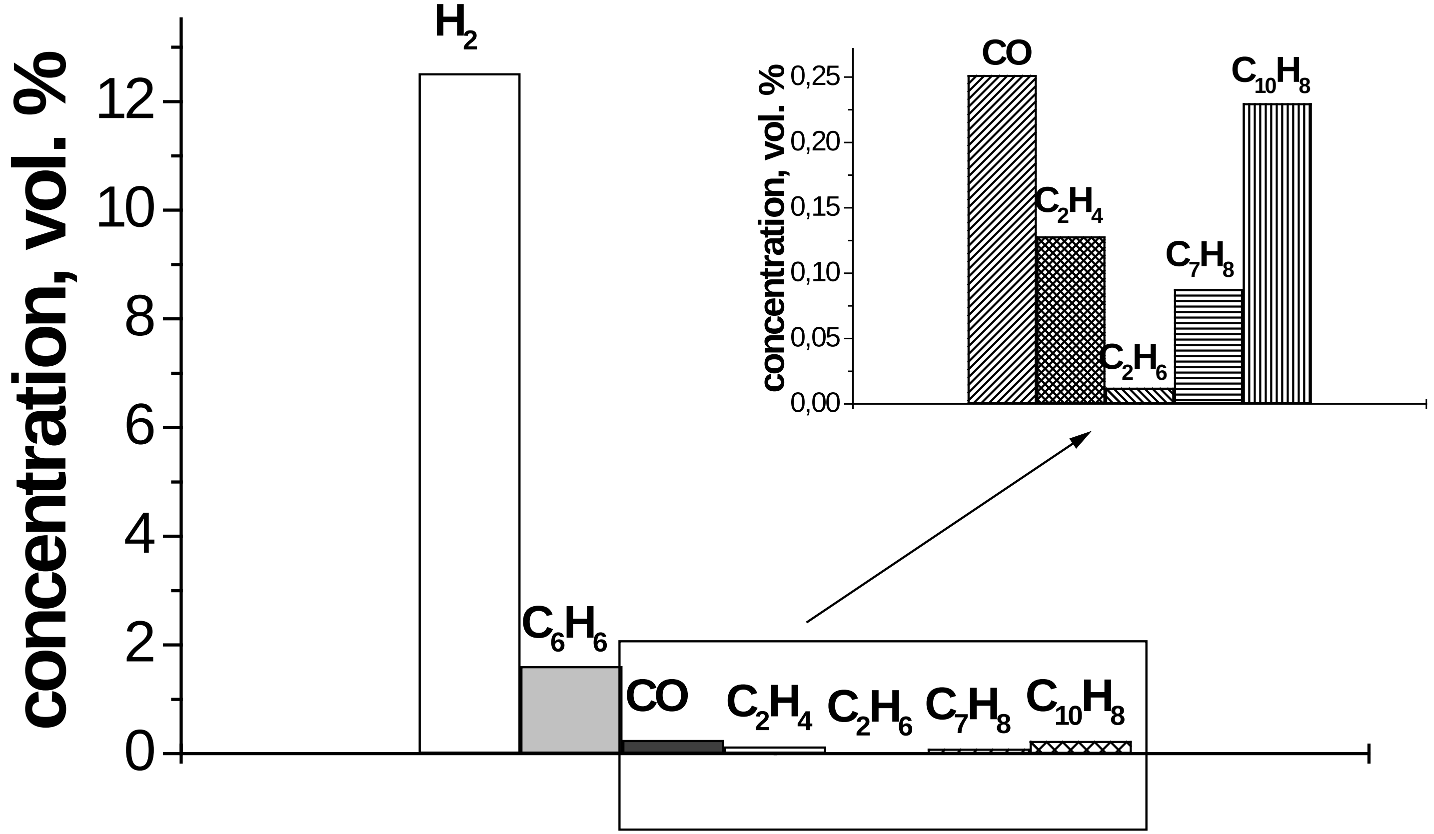
Catalytic activity of Mo/ZSM-5 catalysts (Si/Al=17) in DHA of methane: dependence on Mo content



The maximum catalytic activity (CH_4 conversion ~ 14%) and benzene formation selectivity (70%) were observed for the samples with 2-5% Mo.

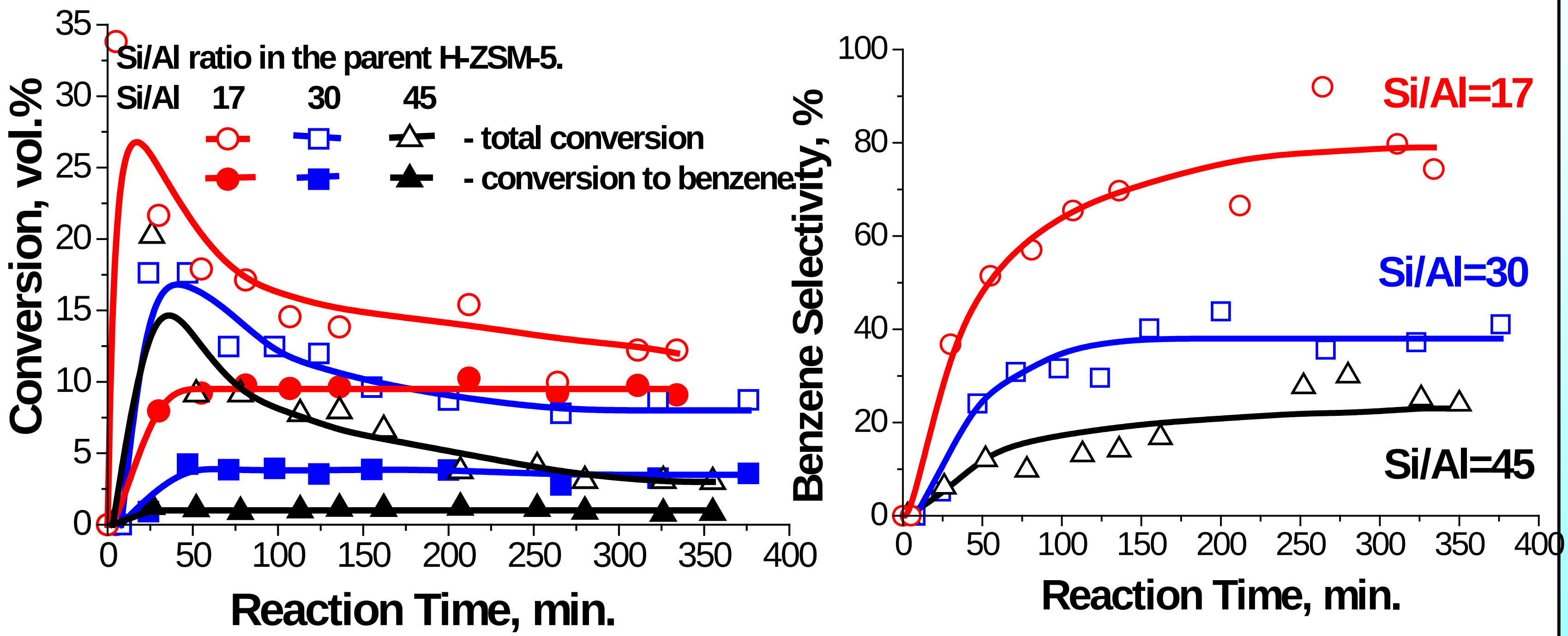
Composition of gaseous reaction products

(2% Mo/ZSM-5 catalyst (Si/Al=17))



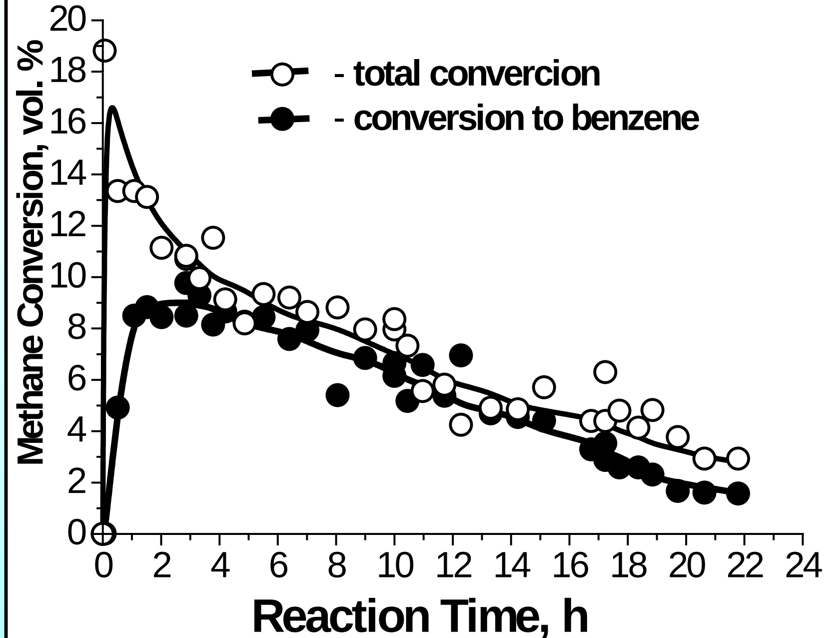
The benzene and hydrogen are main products.

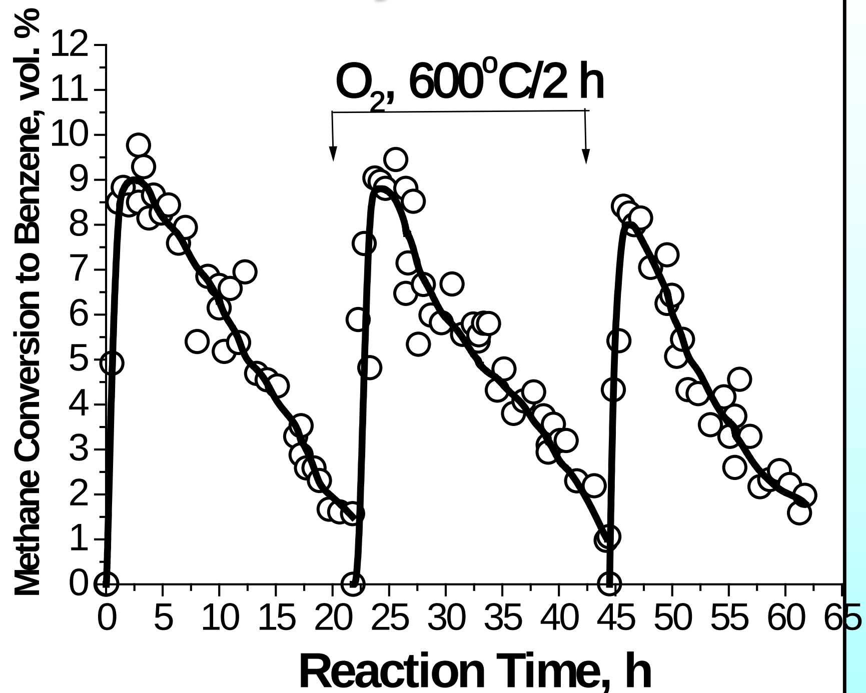
Catalytic activity of 2% Mo/ZSM-5 catalysts in DHA of methane: dependence on Si/Al ratio



The activity and selectivity increase with Si/Al change from 45 to 17.

Catalytic activity of 2% Mo/ZSM-5 catalyst (Si/Al=17) in DHA of methane: stability

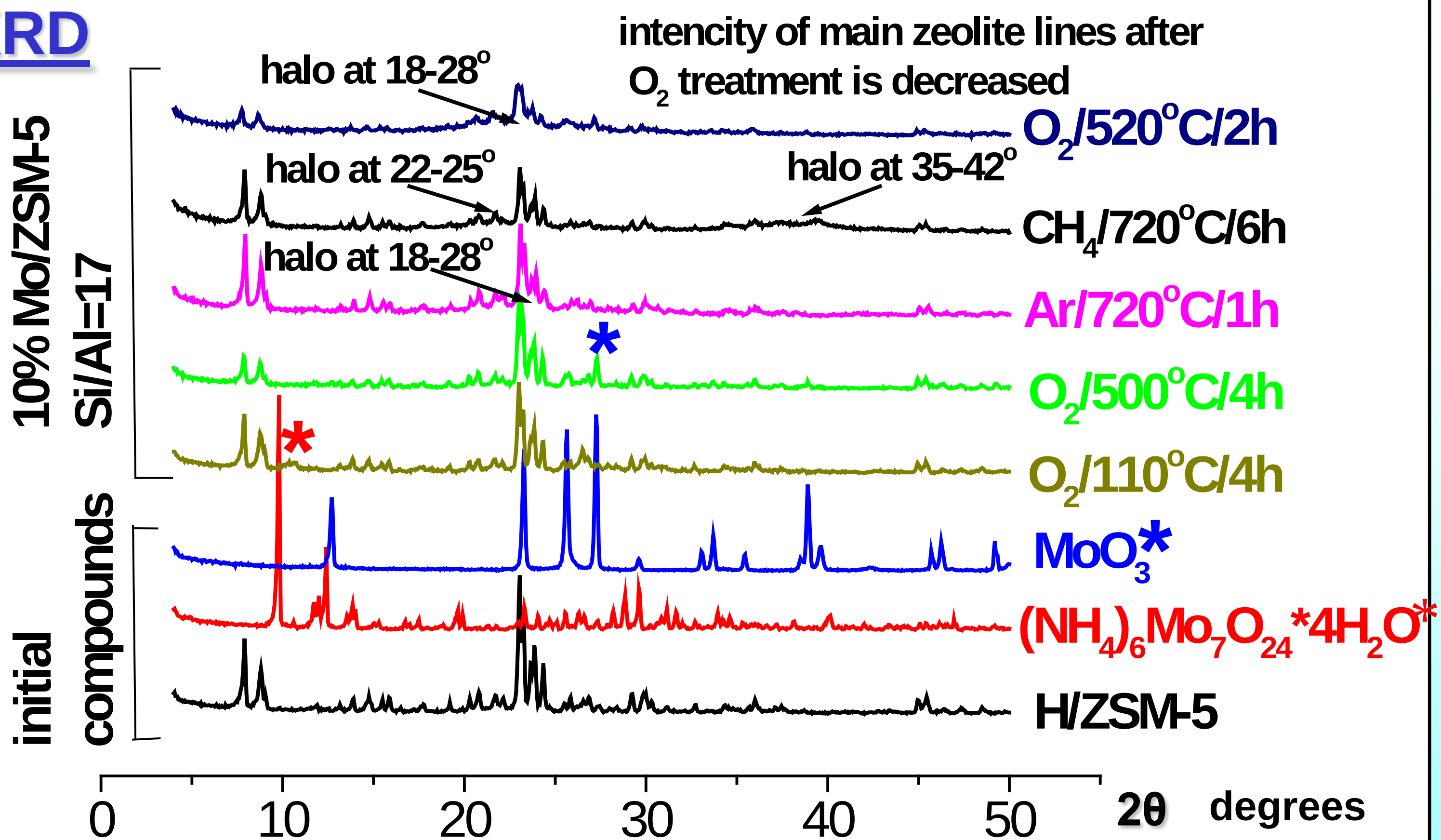




The catalyst performance is decreasing with time on methane stream.

The oxygen treatment with following methane re-admission leads to recovery of catalyst performance.

XRD

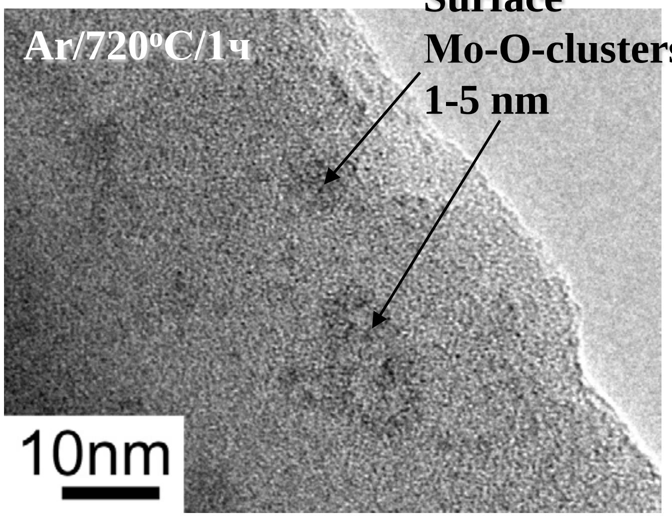


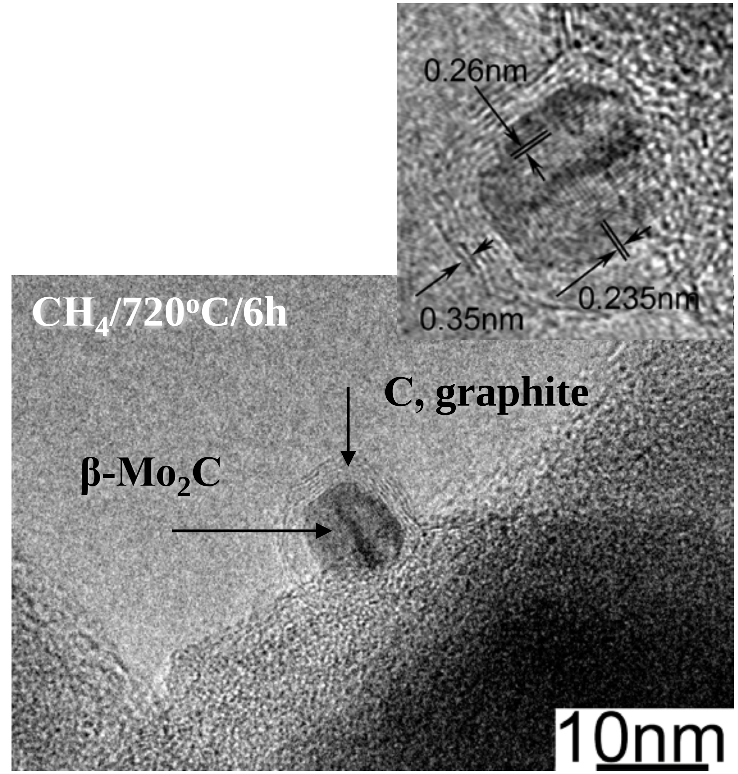
$$(NH_4)_6Mo_7O_{24}{*}2H_2O/ZSM\text{-}5 \xrightarrow{O_2/500^oC} MoO_3/ZSM\text{-}5 \xrightarrow{Ar/720^oC} Mo_9O_{26} \text{ or } Mo_4O_{11}/ZSM\text{-}5$$

CH$_4$/720^{o}C

$$Mo_9O_{26} \text{ or } Mo_4O_{11}/ZSM\text{-}5 \xleftarrow{O_2/520^oC} \eta\text{-}MoC \text{ or } \eta\text{-}Mo_3C_2\ /ZSM\text{-}5$$

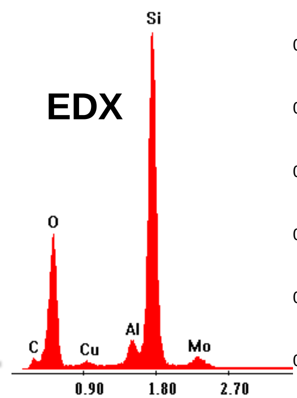
HRTEM (2% Mo/ZSM-5)

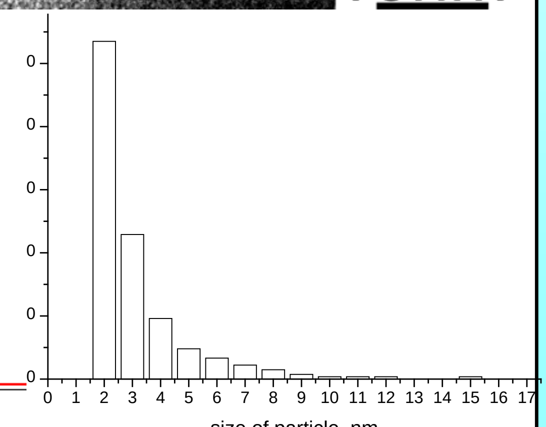




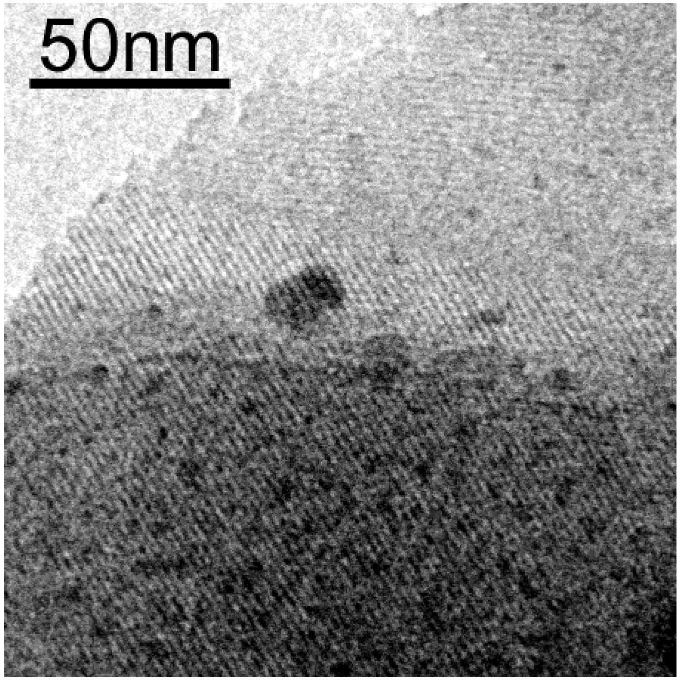
During the reaction, particles of β-Mo_2C with sizes 2-15 nm are forming on the ZSM-5 surface.

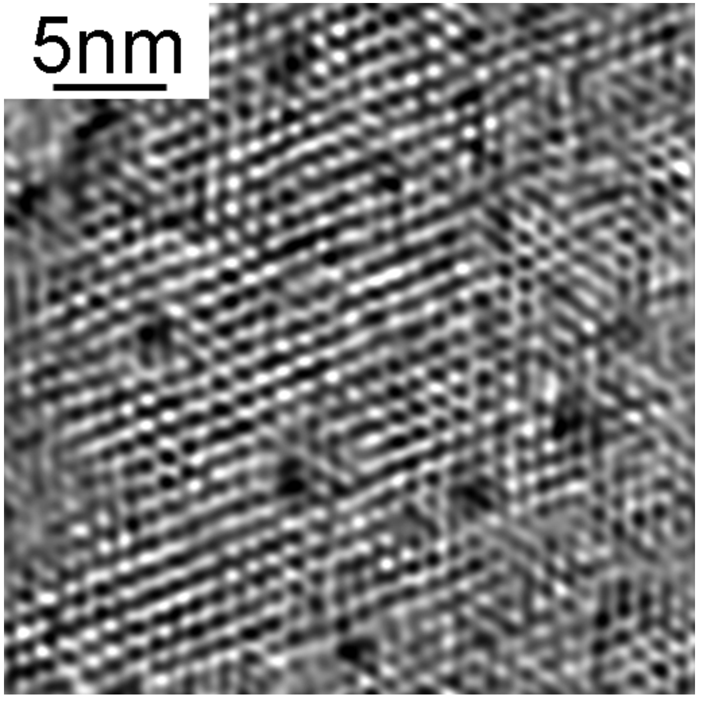
The surface of Mo_2C particle is covered by graphite layers with thickness of ~ 2 nm.





HRTEM (10% Mo/ZSM-5 , CH_4/720ºC/6h)

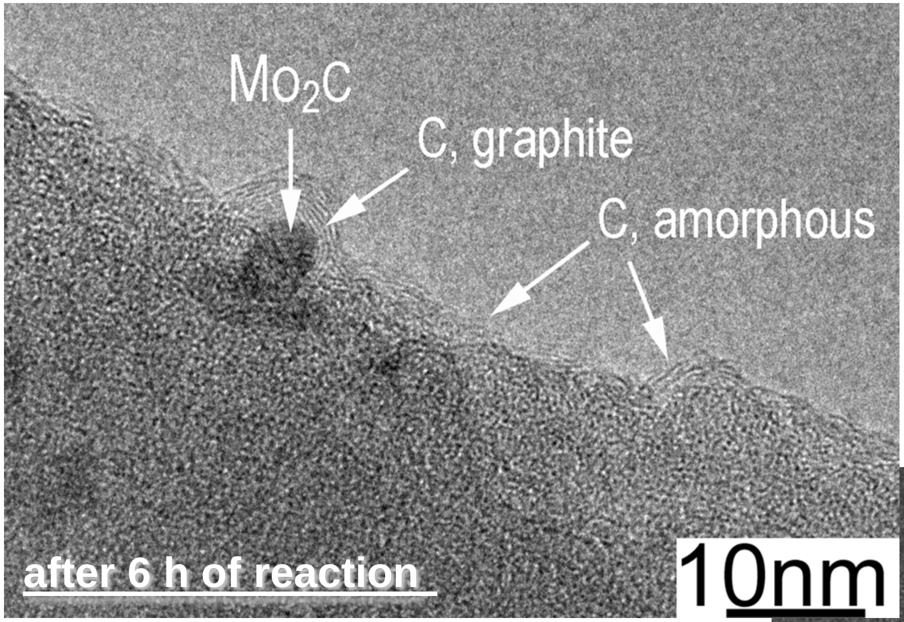




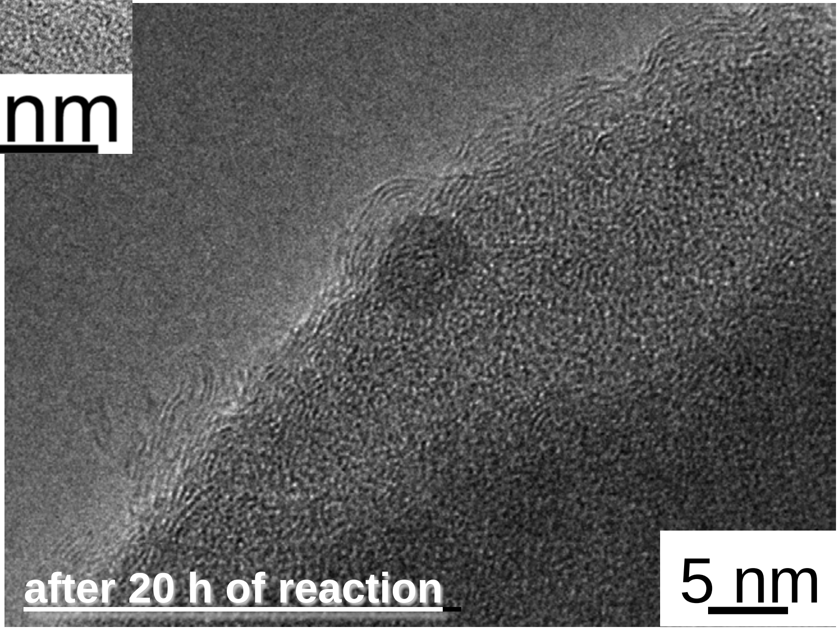
The particle number density on a flat projection of zeolite crystal grows with an increase of crystal thickness, and these particles are absent on the side projections of zeolite crystal.

During the reaction, Mo-containing clusters with sizes ~ 1 nm are forming in the ZSM-5 channels.

HRTEM (2% Mo/ZSM-5, CH_4/720°C)

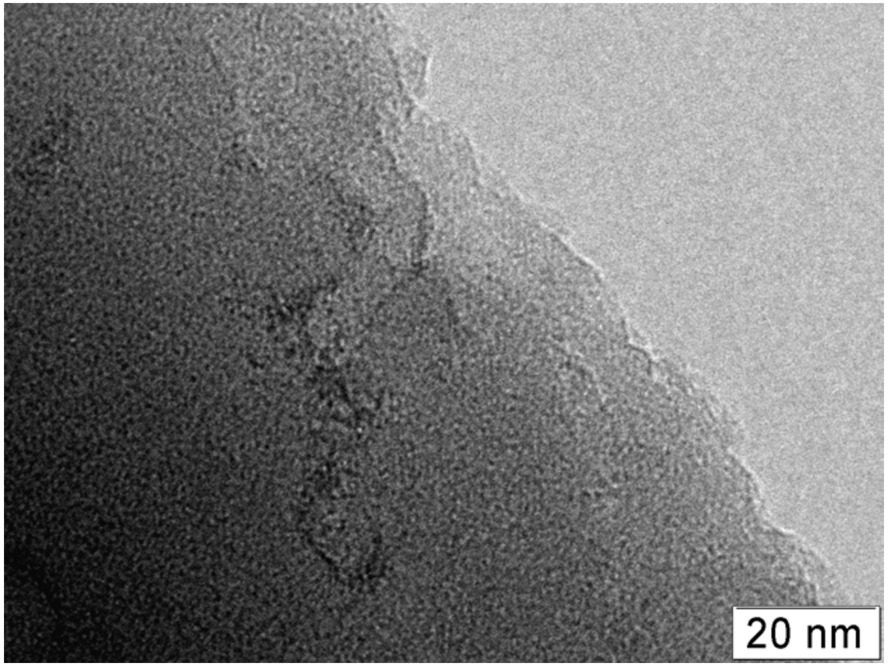


During the reaction, carbonaceous deposits are forming on the ZSM-5 surface in the form of friable disordered layer with thickness up to 3 nm.



The content of friable carbonaceous deposits is increasing with time on stream.

HRTEM (2% Mo/ZSM-5, O_2/520^{o}C/2h)

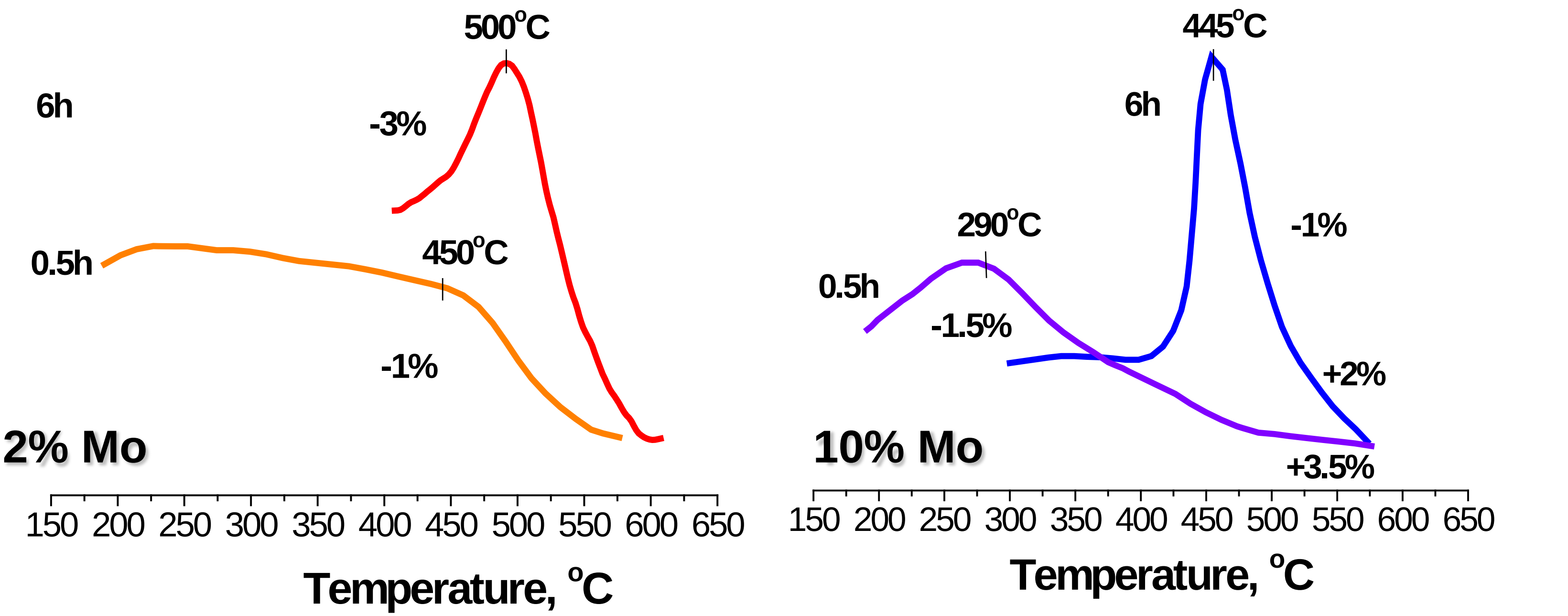


The treatment of the Mo/ZSM-5 catalyst in oxygen stream at 520^{o}C for 2 h leads to formation of Mo-O-contained clusters on zeolite surface similar to those in parent Mo/ZSM-5 catalysts.

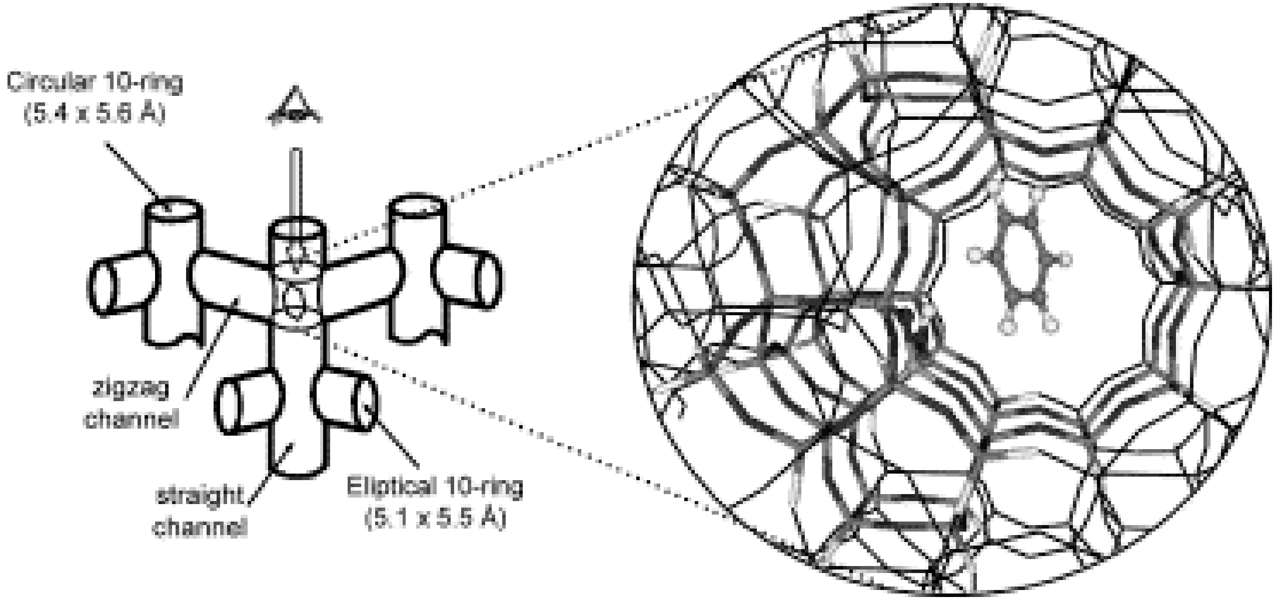
DTA

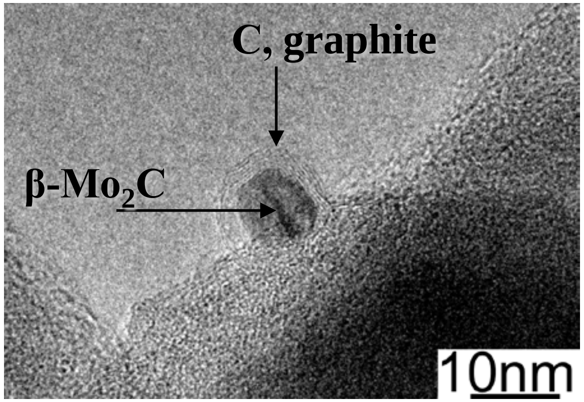
$C_xH_y + (x+y/4)O_2 = xCO_2 + y/2H_2O$ (weight loss)

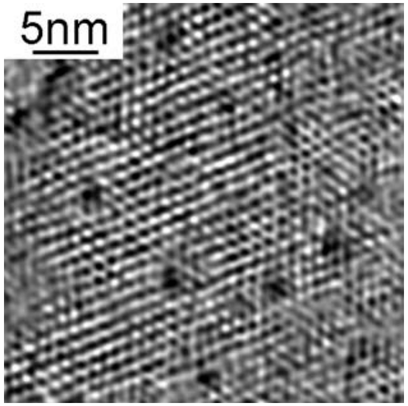
$Mo_2C_{(204\ g/mol)} + 4\ O_2 = 2\ MoO_{3\ (288\ g/mol)} + CO_2$ (weight gain)



For the 2 and 10% Mo/ZSM-5 catalysts and reaction duration between 0.5 and 6 h, carbonaceous deposits in the catalysts with Si/Al = 17 are characterized by a single maximum of the exothermal burn-out effect. The content of carbonaceous deposits and extent of their condensation degree (C/H ratio) are increasing with time-on-stream.







The Mo-containing clusters localized in zeolite channels can be the active centers for DHA of CH_4.

Conclusions:

1. The maximum values of Mo/ZSM-5 catalytic activity (total CH_4 conversion (14%) and C_6H_6 formation selectivity (70%) are achieved at Mo content 2-5% and are increasing upon the lowering of zeolite Si/Al ratio from 45 to 17.

2. Using the HRTEM it was shown, that during the reaction molybdenum carbide β-Mo_2C is formed on the ZSM-5 surface, and it is characterized by the lattice parameters d_{002} = 0.235 nm, d_{400} = 0.26 nm and the particle size of 2-15 nm. It was also demonstrated, that during the reaction Mo-containing clusters with sizes ~ 1 nm are forming in the ZSM-5 channels.

3. In the course of reaction, the carbonaceous deposits are formed both on the surface of Mo_2C particles (in the form of graphite layers with lattice parameter d_{002} = 0.35 nm and thickness of approximately 2 nm) and on the zeolite surface (in the form of friable disordered layer with thickness up to 3 nm).

4. The content of carbonaceous deposits and extent of their condensation (C/H ratio) are increasing with time-on-stream.

5. The oxygen treatment with following methane re-admission leads to recovery of catalyst performance.

Acknowledgements:

The authors are grateful to Dr. V.A. Ushakov for the XRD measurements and discussion, Dr. G.S. Litvak for the DTA measurements.