INTAS Workshop 2007
Mid-term review of the INTAS Thematic Calls 2005
on Genomics/Proteomics & Energy

NEW WAYS OF HYDROGEN GENERATION FROM NATURAL GAS

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   - Catalytic way of hydrogen production
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Hydrogen as a fuel of future

Hydrogen is a clean and very effective burning fuel: $2H_2 + O_2 = 2H_2O$

hydrogen	120 GJ/ton
gasoline	45 GJ/ton

Demand for hydrogen is increasing on ~10-15% per year:

refining industries (desulfurization, hydrotreating)
chemical processing (hydrogen peroxide, NH_3, hydrogenation reaction)
electronics
food processing (hydrogenation of fats and oils)
metal manufacturing

Feedstocks for hydrogen production:

natural gas
petroleum
coal
electrolysis

Catalytic way of hydrogen production

Natural gas (> 90% CH_4) is the main source for production of hydrogen.

Methane

Steam reforming of methane → **$H_2 + CO$**

$CH_4 + H_2O = 3H_2 + CO$ **T = 800-1000°C, P = 1.5-3 MPa**

$CO + H_2O = CO_2 + H_2$

Catalytic decomposition of methane → **$H_2 + C_{nanotube}$**

$CH_4 = 2H_2 + C$ **T = 500-700°C, P = 0.1 MPa**

$C + H_2O = CO + H_2$

Methane dehydroaromatization → **$H_2 + C_6H_6$**

$6CH_4 = 9H_2 + C_6H_6$ **T = 700-750°C, P = 0.1 MPa**

$CH_4 = 2H_2 + C$

$C + H_2O = CO + H_2$

Methane dehydroaromatization (CH_4 DHA)

over Mo/ZSM-5 catalysts – a new promising environmentally-friendly way to obtain both **hydrogen** and valuable aromatics.

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

9 mol H_2/1mol C_6H_6

Selectivity of benzene formation ~ 80%.

$MoO_z \overset{CH_4}{=>} Mo_2C$ (or MoO_xC_y) — **H-ZSM-5**

$$\mathbf{CH_4} \underset{+H_2}{\overset{-H_2}{\leftrightarrow}} CH_x \leftrightarrow C_2H_y \leftrightarrow \textbf{aromatic hydrocarbons}$$

$\downarrow$ (from CH_x and from aromatic hydrocarbons)

carbonaceous deposits + H_2

Catalytic dehydroaromatization of CH_4

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.

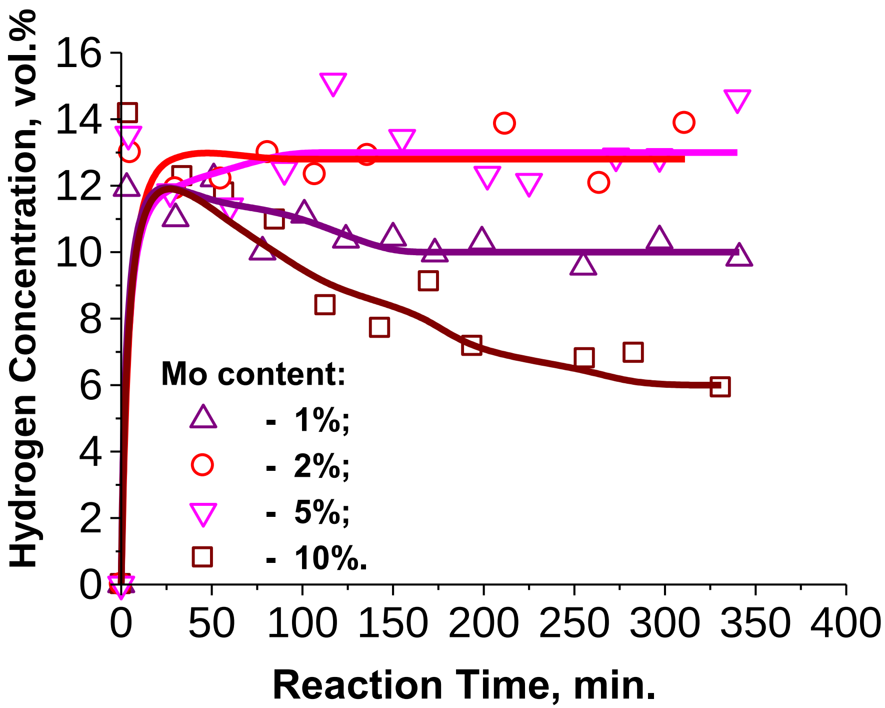
Reaction conditions:

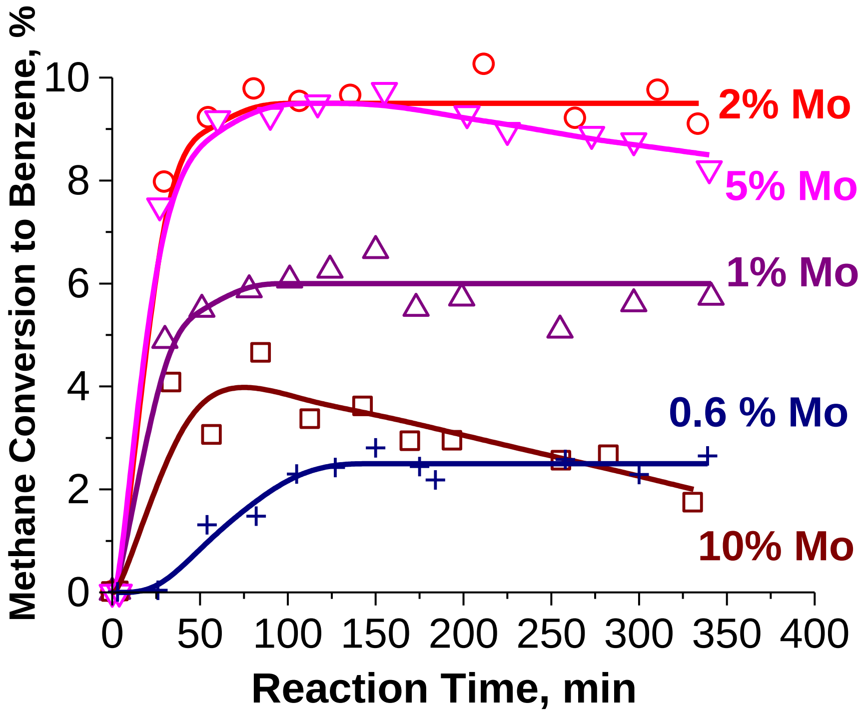
$90\%CH_4 + 10\%Ar$;
T = 720°C;
GHSV = 810 h^{-1}.
load = 1.0 cm^3 (0.6 g);
fraction = 0.25-0.5 mm.

Methods:

XRD, N_2 adsorption, HRTEM, EDX, DTA,TG, ESR studies

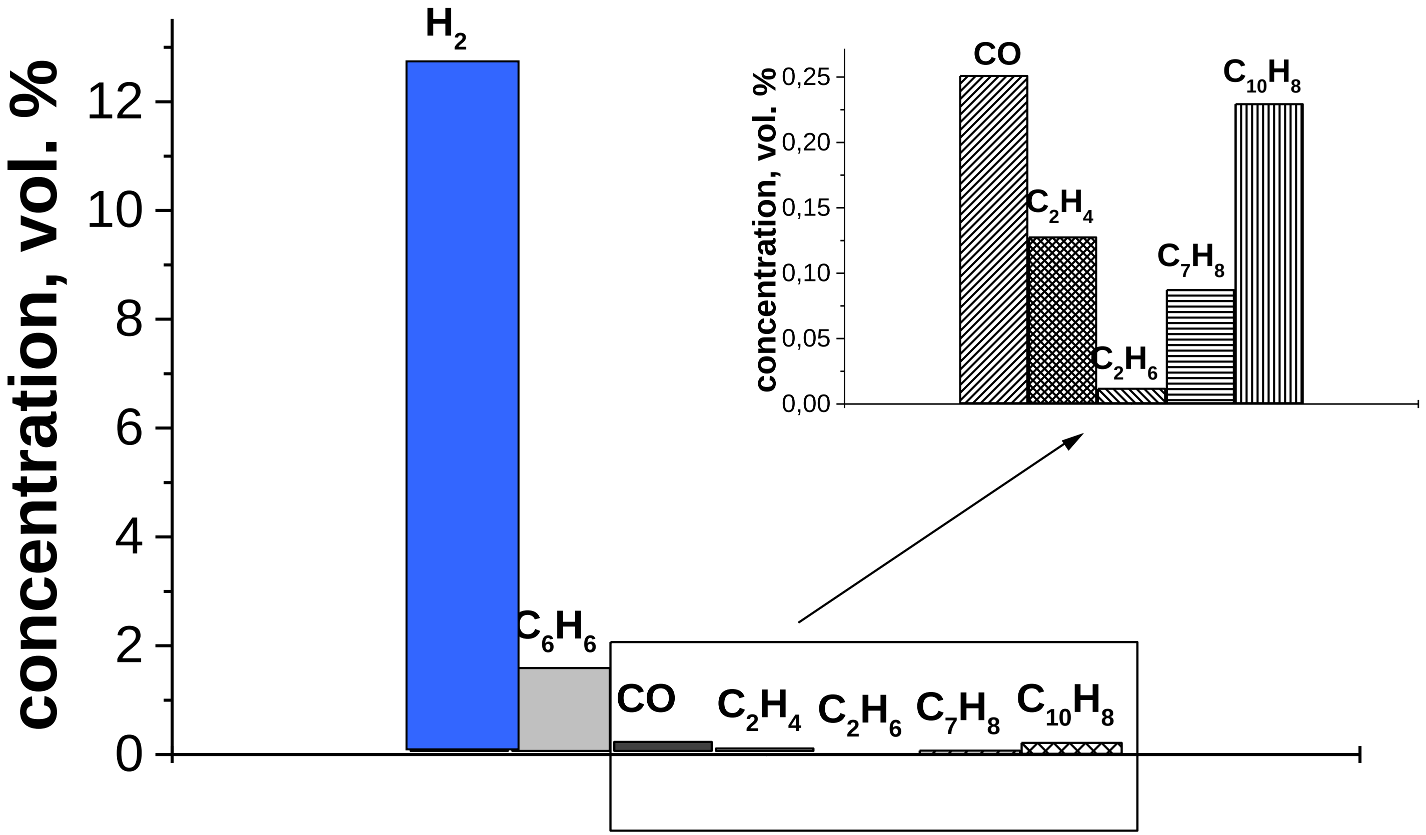
Hydrogen production on Mo/ZSM-5 catalysts in CH_4 DHA: dependence on Mo content





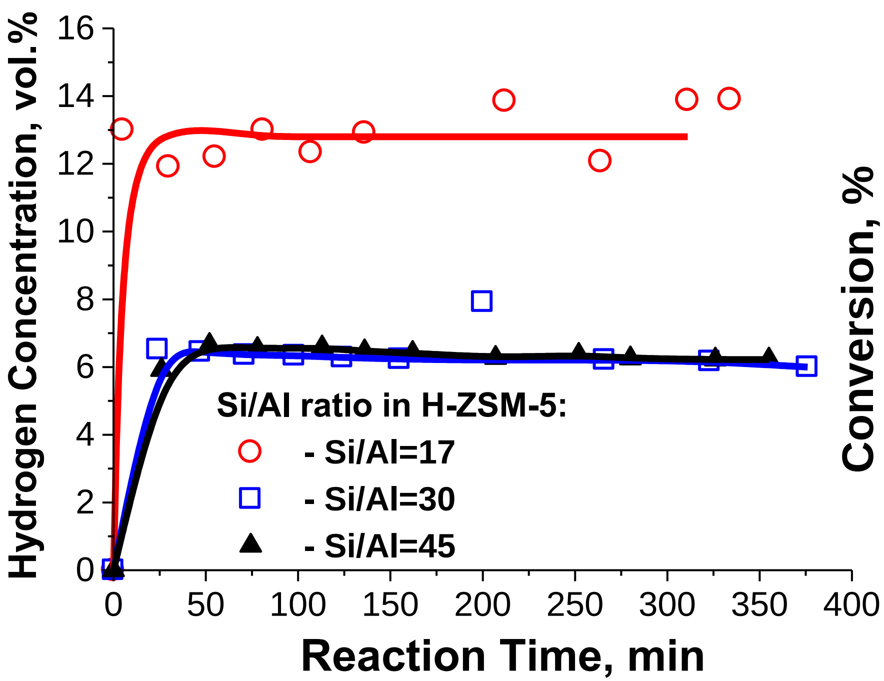
The Mo/ZSM-5 catalyst has high activity in CH_4 DHA reaction.
The maximum value of hydrogen production is observed at 2-5% Mo content.

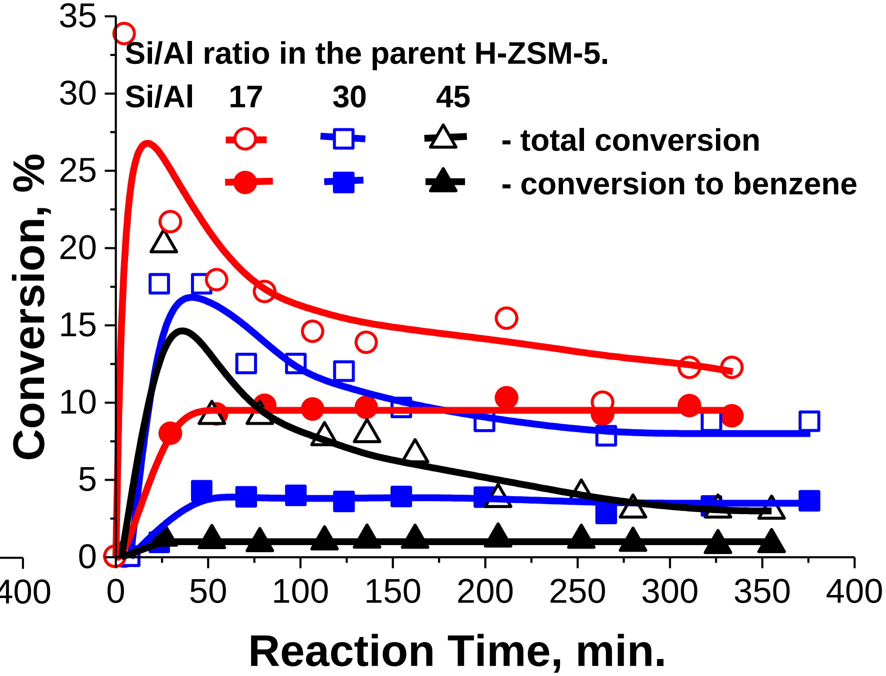
Composition of gaseous reaction products
(2%Mo/ZSM-5 catalyst with Si/Al=17)



The hydrogen and benzene are main products.

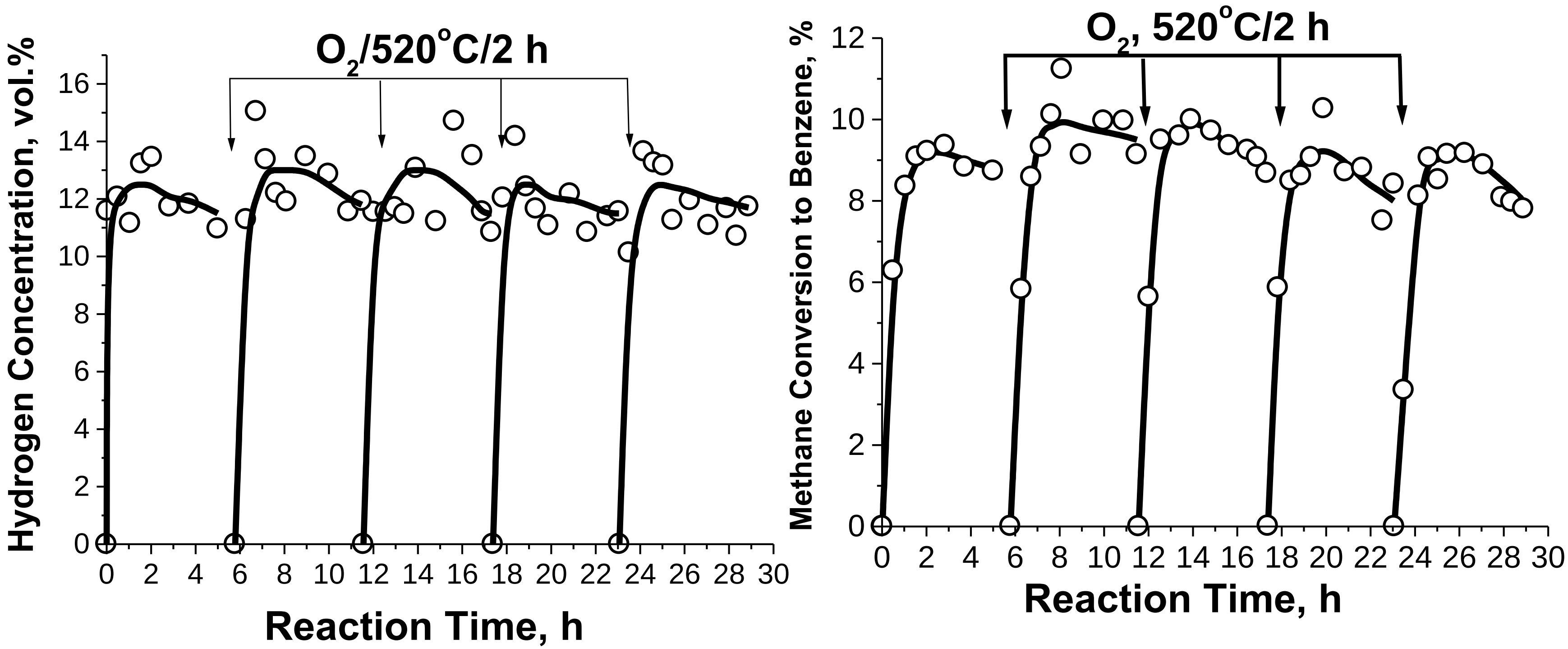
Hydrogen production on Mo/ZSM-5 catalysts in CH_4 DHA: dependence on Si/Al ratio





The maximum value of hydrogen production on 2%Mo/ZSM-5 catalyst is observed at Si/Al = 17.

Hydrogen production on 2%Mo/ZSM-5 catalysts in CH_4 DHA: reaction/regeneration



Selected oxidative treatment conditions of coked Mo/ZSM-5 providing stable performance of the catalysts under multiple reaction-oxidative treatment cycles.

CH_4 dehydroaromatization : economic aspect

Compound	Cost	Productivity of catalyst in CH_4 DHA	Balance, euro
Natural Gas	100 euro/$10^3 m^3$	10^3 m^3	-100
Benzene	1200 euro/ton	0.4 tons	+480
Hydrogen	270 euro/$10^3 m^3$	1.4*10^3 m^3	+380

Total + ~750euro/$10^3 m^3$ converted gas

CH_4 dehydroaromatization over Mo/ZSM-5 catalysts

Advantages:

- The produced hydrogen is absolutely free of CO and CO_2.
- No need for PROX and SHIFT reactions
- Benzene formation gives substantial additional value
- Technology feasibility is obvious.

State-of-the-art:

- the optimal formula of Mo/ZSM-5 catalyst;
- the activity and stability of Mo/ZSM-5 catalyst in DHA CH_4 vs. preparation and reaction condition;
- the nature of carbonaceous deposits;
- the regeneration and recycling condition.

Tasks:

- To increase hydrogen production capacity by introduction of a second metal into Mo/ZSM-5 catalyst;
- To optimize regeneration conditions in pilot plant conditions
- To build and operate demonstration plant; scale up.

Catalytic methane decomposition on Ni- and Fe-containing catalyst as an alternative method for **hydrogen production** from natural gas.

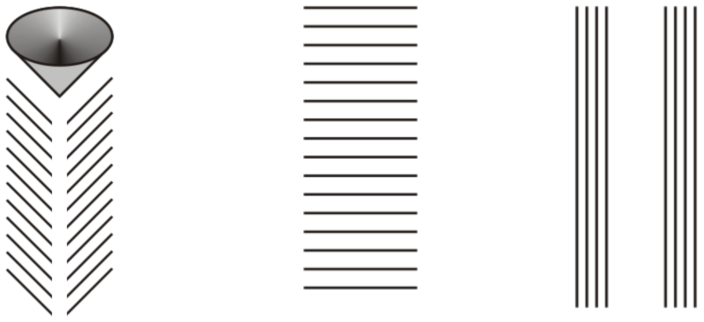
$$CH_4 \Rightarrow 2H_2 + C_{nanotube} \qquad 2molH_2/1molC$$

Reaction conditions:

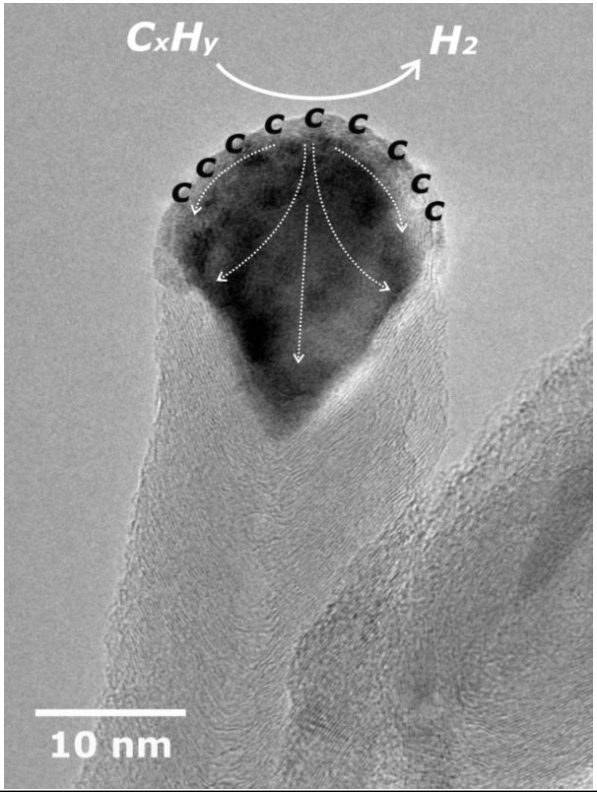
- **Temperature: 500 – 700 °C;**
- **Catalyst: Ni, Co, Fe, alloys.**

Products:

- **Hydrogen;**
- **Mesoporous nanostructured carbon material (nanofibers and nanotubes).**



"fishbone" *"platelet"* *nanotubes*



Hydrogen production by catalytic CH_4 decomposition

Preparation of catalysts:

Method of co-precipitation of aqueous solutions of appropriate metal nitrate ($Ni(NO_3)_2$, $Cu(NO_3)_2$, $Fe(NO_3)_3$ and $Al(NO_3)_3$) at controlled value of temperature.

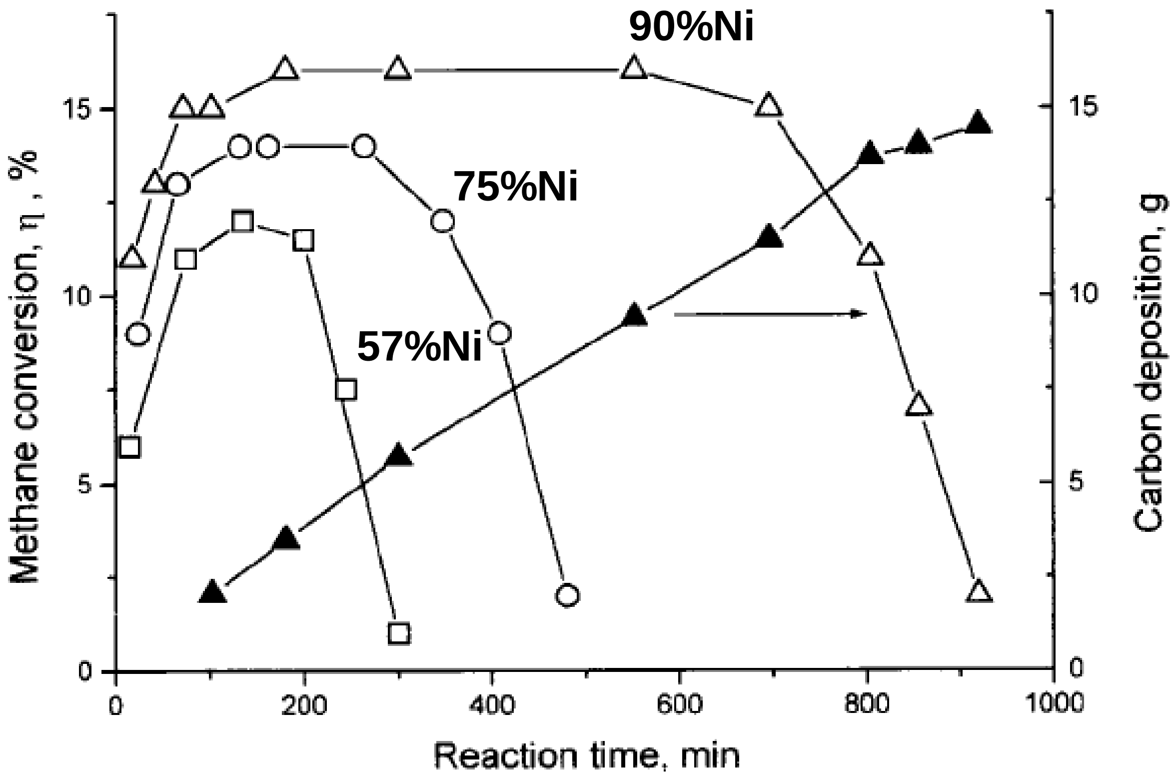
Reaction conditions:

100%CH_4
T = 550-625^oC;
V_{CH4} =0.045-0.120 m^3/g_{cat}*h;
load = 0.1 g;
fraction = 0.25-0.5 mm.

Methods of catalyst characterization and control:

XRD, N_2 adsorption, HRTEM, EDX, DTA,TG, ESR, EXAFS

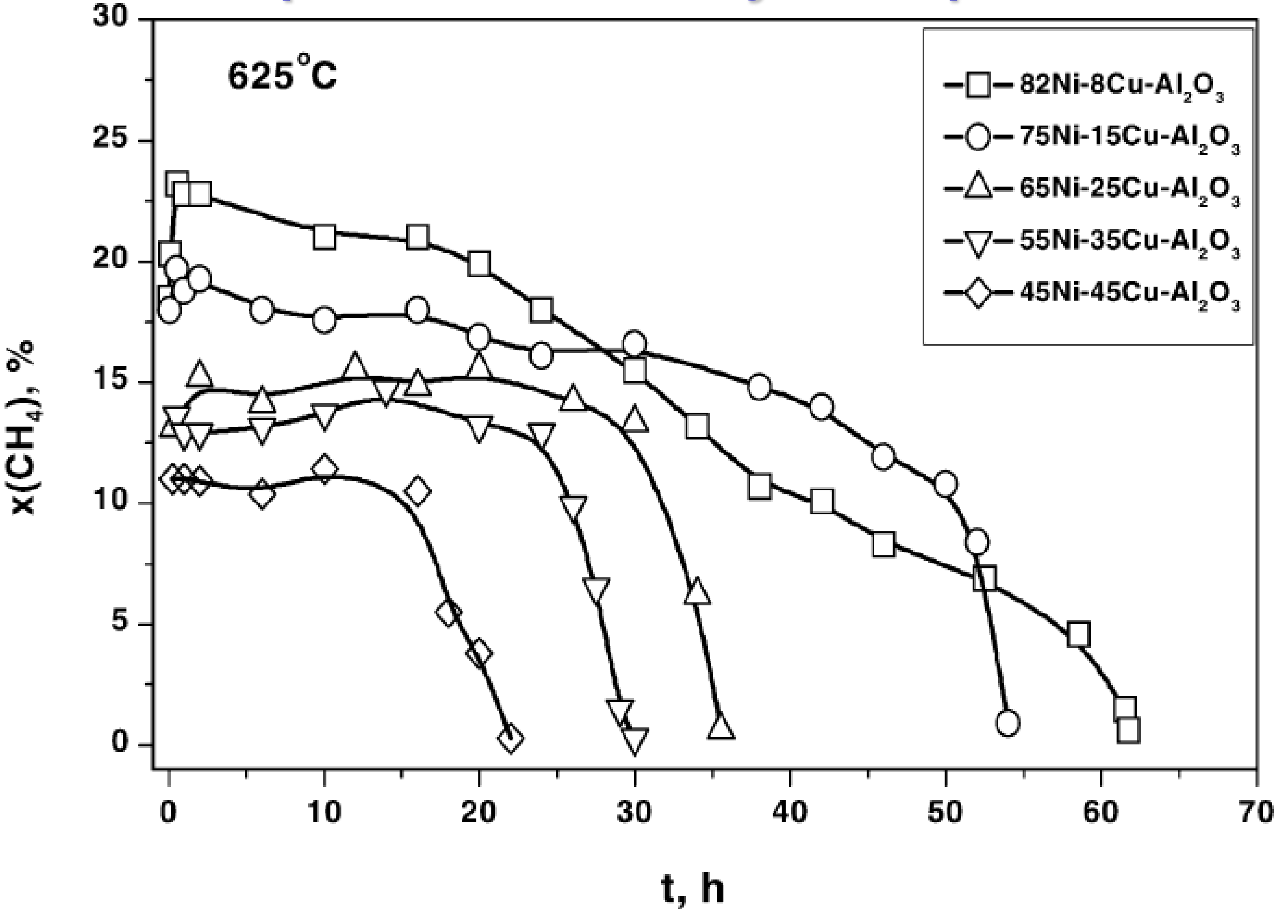
The Ni-Al catalysts in CH_4 decomposition to hydrogen and CNF: dependence on Ni content



T = 550°C, P_{CH4} = 100 kPa, space velocity 0.120 m^3/g_{cat}*h, sample weight 0.1 g

The Ni-Al_2O_3 catalyst has high activity in CH_4 decomposition. The maximum value of catalytic activity is observed at 90%Ni content.

The Ni-Al catalyst in CH_4 decomposition to hydrogen and CNF: dependence on catalyst composition



T = 625°C, P_{CH4} = 100 kPa, space velocity 0.120 m^3/g_{cat}*h, sample weight 0.1 g

The Ni-Cu-Al_2O_3 catalysts have high stability in CH_4 conversion. The best performance is observed at 82Ni-8Cu-10Al_2O_3 composition.

Hydrogen production in catalytic CH_4 decomposition (T = 625°C)

Catalyst	χ_{CH4}, %	τ, h	G, g_C/g_{cat}	ΣH_2, $m^3H_2/g_{cat.}$	Hydrogen productivity, $10^3 m^3 H_2/kg_{cat.}$*h
90Ni-Al_2O_3	31	2	22.4	0.112	0.0056
82Ni-8Cu-Al_2O_3	22	61.5	515	2.435	0.040
75Ni-15Cu-Al_2O_3	18	54	430	1.746	0.032
62Fe-8Ni-Al_2O_3	22	64	145	0.591	0.009

Catalytic CH_4 decomposition: economic aspect

Compound	Cost	Productivity of catalyst in CH_4 decomposition	Balance, euro
Natural Gas	100 euro/$10^3 m^3$	10^3 m^3	-100
Carbon nanotubes	$35*10^6$ euro/ton	0.5 tons	**0,0** $+17.5*10^6$
Hydrogen	270 euro/$10^3 m^3$	$2*10^3$ m^3	+540

Total **+ 440**

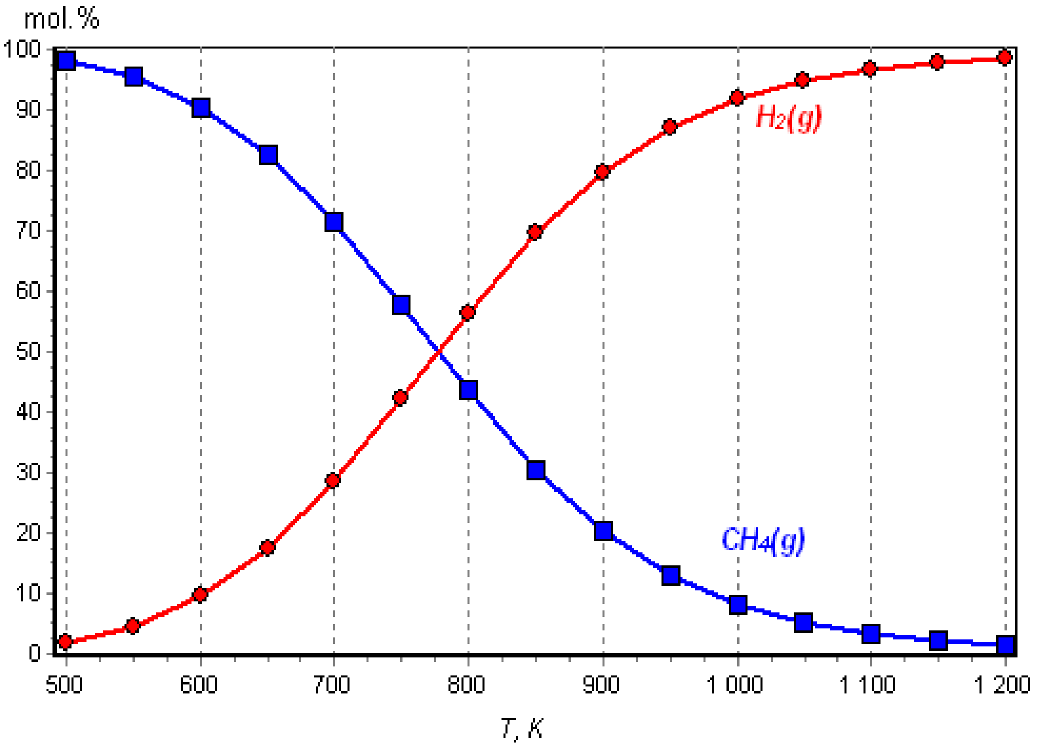
+ ~$17.5*10^6$ euro/$10^3 m^3$ converted gas

Thermodynamic data for reaction $CH_4 \Rightarrow 2H_2 + C$

T, K	$\Delta_r H^o_T$, kJ/mol	$\Delta_r G^o_T$, kJ/mol	$K_{equilibrium}$	CH_4 conversion to H2 and C, vol.%
900	70.6	-8.6	3.2	66.3

Equilibrium composition of gaseous mixture at 900 K:

H_2 79.7 vol.%
CH_4 20.3 vol.%



Catalytic CH_4 decomposition to hydrogen and CNF

Advantages:

-The produced hydrogen is absolutely free of CO and CO2.
- No need for PROX and SHIFT reactions
- The CNF, MWCNT and SWCNT production gives substantial additional value
- Technology feasibility is obvious

State-of-the-art:

- the optimal formula of Ni-Al, Ni-Cu-Al, Fe-Ni-Al catalysts
- the activity of catalyst and kinetics of methane decomposition vs. preparation and reaction conditions;
- the structure of carbonaceous materials CNF and MWCNT.

Tasks:

- To optimise regeneration condition
- To find natural materials as catalysts for industrial scaling up

Conclusions:

1. The methane dehydroaromatization and catalytic decomposition of methane are promising ways to produce hydrogen from natural gas.

2. The produced hydrogen is absolutely free of CO and CO2.

3. No need for PROX and SHIFT reactions.

4. Benzene and CNF formation gives substantial additional value

5. There are several tasks for International projects.

Thank you

for your attention

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DHA CH_4

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