TARGET COMPREHENSIVE PROGRAM OF SCIENTIFIC RESEARCH OF NAS OF UKRAINE

Development of scientific principles of obtaining, storage and use of hydrogen in autonomous energy supply systems

DEVELOPMENT O F NANOSTRUCTURED CATALYSTS AND NEW TECHNOLOGICAL SOLUTIONS FOR THE PROCESSING OF BIOGAS WITH THE PRODUCTION OF HYDROGEN FUEL FOR THE METHANE CONVERSION UNIT OF HIGH-TEMPERATURE FUEL CELLS

Project No.21-21

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Purpose of research on the project:

- *determination of the role of modifying additives/promoters of different nature in the Ni/Al_2O_3 compositions on monolithic ceramic supports, structural and dimensional factors, functional properties of the surface as regulating factors of stable operation of catalysts in the process of biogas reforming;*
- *development of a method for preparation of aforementioned catalytic compositions to ensure their operation performance (thermal stability, resistance to oxidation/reduction, the action of sulfur-containing compounds, carbonization, etc.) in the target processes;*
- *determination of conditions for plasma-catalytic reforming of biogas in the presence of metal oxide Ni/Al_2O_3 and zeolite catalysts*

The main tasks of the project:

- elucidation of the nature of the influence of additives of alkali, rare-earth metal compounds on the activity and selectivity of $Ni\text{-}Al_2O_3$ /cordierite catalysts in the processes of steam, carbon dioxide conversion and combined reforming of biogas;

- *optimization of the composition of catalysts on block supports of honeycomb structure to ensure their high resource characteristics (productivity, resistance to carbonization, the action of sulfur-containing compounds)*
- *determining the conditions for the implementation of reforming processes in a high-performance mode, including combined (steam-oxygen, oxy-steam-carbon dioxide conversion), with high yields of hydrogen/SG with an adjustable ratio of H_2/CO;*
- *elucidating the possibility of implementation of biogas reforming on metal-oxide Ni/Al_2O_3 and zeolite catalysts in plasma-catalytic regime*

Biogas: 50–87% of methane, 13–50% of CO_2, admixtures of H_2, H_2O, ***H_2S;***

- a strategically important raw material for the producing synthesis gas / hydrogen for the obtaining industrially important products and motor fuels; as energy sources for fuel cells

Possible ways of biogas processing:

- carbon dioxide conversion of methane (CDCM)

$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$ ($\Delta H° = +247$ kJ/mol) (1)

- steam reforming of methane (SRM)

$CH_4 + H_2O \leftrightarrow CO + 3H_2$ ($\Delta H° = +206$ kJ/mol) (2)

- partial oxidation of methane (POM)

$CH_4 + 0{,}5O_2 \leftrightarrow CO + 2H_2$ ($\Delta H° = -35{,}6$ kJ/mol) (3)

- water gas shift reaction (WGSR)

$H_2 + CO_2 \leftrightarrow H_2O + CO$ ($\Delta H° = -39{,}5$ kJ/mol) (4)

- Boudoir reaction

$2CO \leftrightarrow CO_2 + C$ ($\Delta H° = -171$ kJ/mol) (5)

- methane cracking

$CH_4 \leftrightarrow 2H_2 + C$ ($\Delta H° = +75$ kJ/mol) (7)

The main method of biogas processing – carbon dioxide conversion of methane

The mechanism of the carbon dioxide conversion of methane on Ni-Al_2O_3 catalysts:

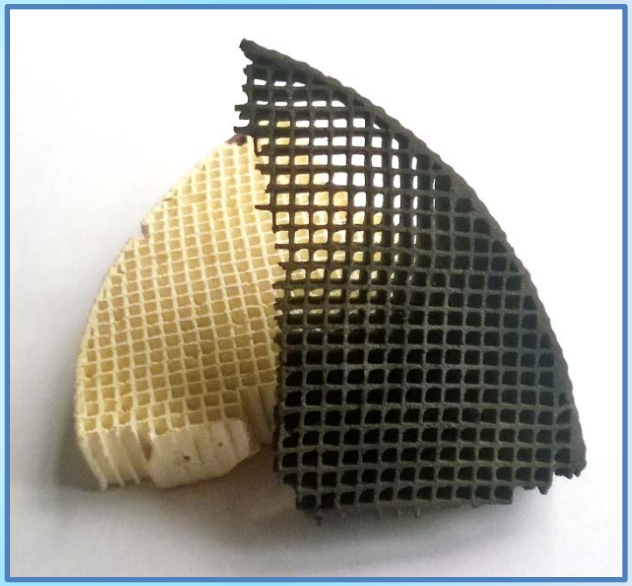
1. $CH_4 + Z \leftrightarrow \{CH_x\}\text{-}Z + (4\text{-}x)H_{ads.} \leftrightarrow Z\text{-}C + 2H_2$,
2. $CO_2 + Z \leftrightarrow Z\text{-}O + CO$,
3. $Z\text{-}C + Z\text{-}O \leftrightarrow Z\text{-}CO + Z$,
4. $Z\text{-}CO \leftrightarrow Z + CO$,

where Z – active center of the catalyst

The main problems:

1. High process temperatures
2. High endothermicity of the process
3. Carbonization of most known catalysts

Developed biogas conversion structured catalysts



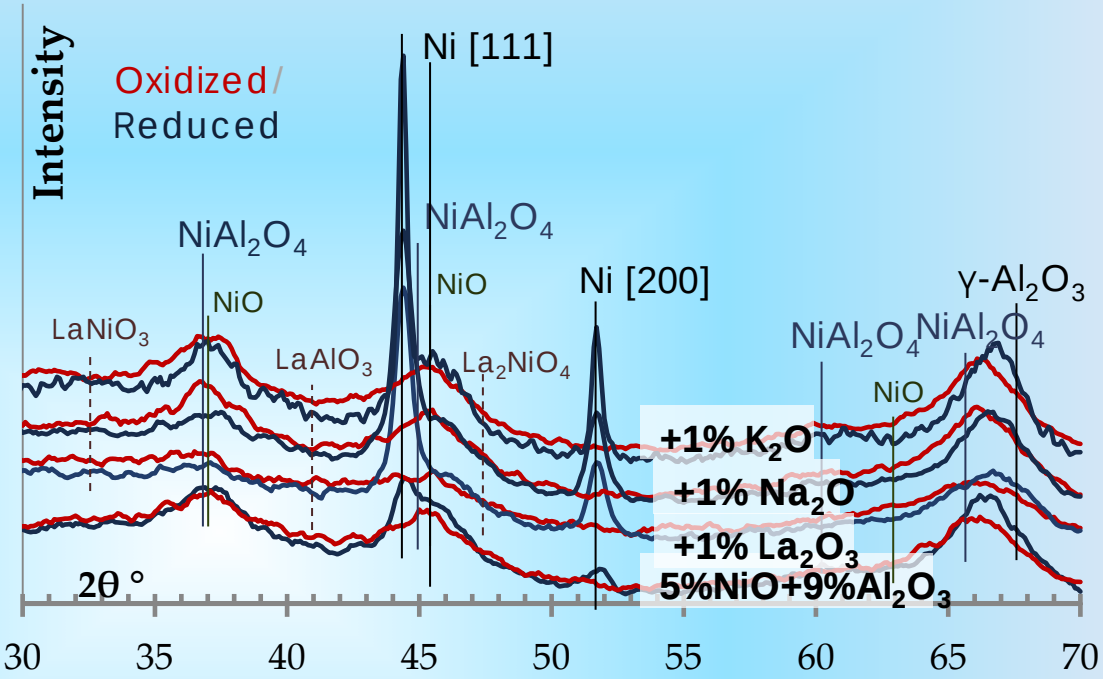
The structural form of the catalyst provides:

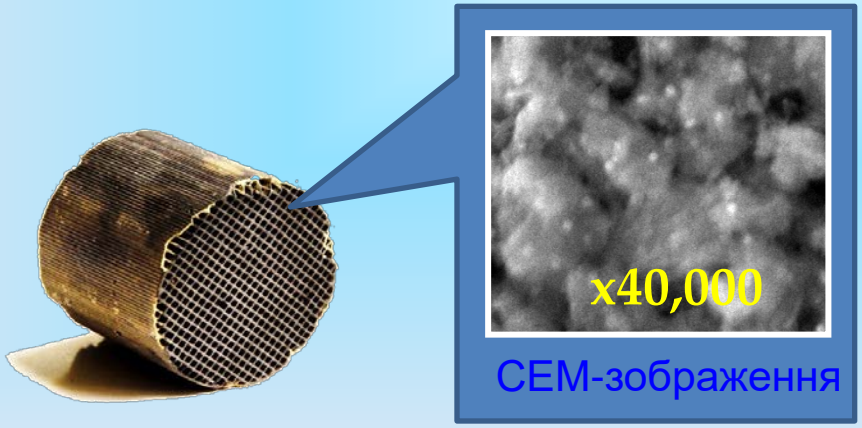
- Increase in the activity and decrease in the pressure drop
- high gas hourly space velocities
- increased thermal stability and mechanical strength
- reduces the likelihood of elemental carbon formation
- enables to optimize the thermal regime of the process

Modification of $Ni\text{-}Al_2O_3$/cordierite catalysts

Modifying additives of different nature:

- La_2O_3
- CeO_2
- K_2O
- Na_2O
- CaO
- MgO





СЕМ-зображення

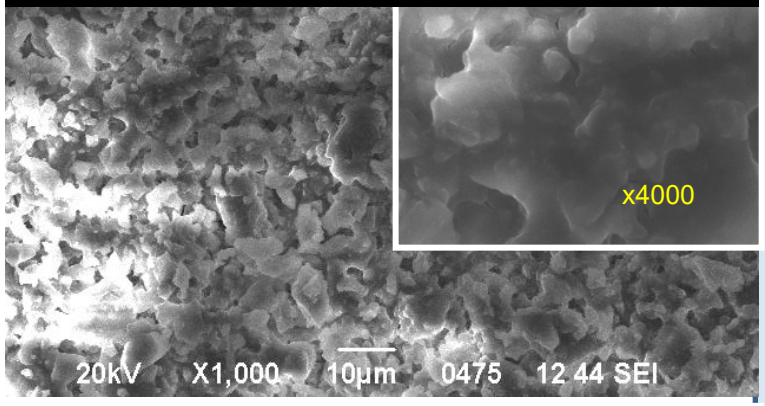
Composition of the applied phase: NiAl= 5%NiO+8%Al_2O_3	CSR, nm	
	Al_2O_3	Ni
NiAl	3,5	24
NiAl+1%CeO_2	3,5	22
NiAl+1%La_2O_3	3,5	12

Catalyst surface morphology

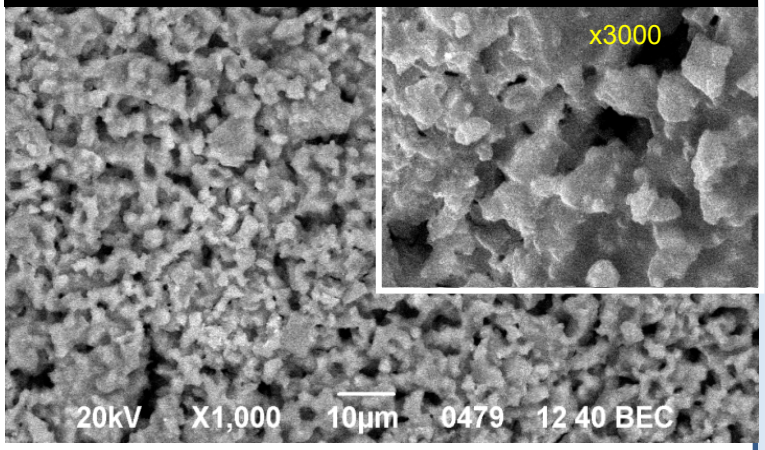
Specific surface area of initial and reduced samples of massive catalysts, m^2/g

94%Al_2O_3 +5%NiO +	Initial catalyst, calcination temperature		Reduced at 750°C catalyst
	650 °C	750 °C	
-	128,5	75,0	70,1
+1%La_2O_3	89,3	73,3	70,6
+1%CeO_2	100,4	81,1	81,2
+1%K_2O	115,8	90,1	86,6
+1%Na_2O	111,0	89,7	88,2
+1%CaO	95,7	82,0	82,3
+1%MgO	87,2	70,9	79,3

5%NiO+4%Al_2O_3/cordierite



5%NiO+4%Al_2O_3+1%La_2O_3/ cordierite



Carbon dioxide conversion of methane

Catalyst composition	Reagent concentration, vol %		Temperature, °C		Max. $X(CH_4)$(%) /T(°C)	Max. conc. prod., vol %	
	CH_4	CO_2	50%	80%		CO	H_2
$5,3\%NiO+5,0\%Al_2O_3+1,6\%CaO$	6,2	8,2		560	99 / 760	12,6	11,9
	6,2*	8,2	495	640	94,5 / 750	11,7	11,8
	3,75	10,1	550	630	94 / 730	7,8	6,3
$4,8\%NiO+5,0\%Al_2O_3+1,2\%MgO$	6,3	8,6	495	575	100 / 730	13,0	12,2
	3,6	10	545	690	86,5 / 730	6,7	5,8
$5,8\%NiO+5,4\%Al_2O_3+1,4\%La_2O_3$	6,6	8,7	600	680	98,5 / 750	13,2	12,8
	4,1	10,2	575	660	96,5 / 710	8,6	7,2
$2,5\%NiO\ 2,0\%Al_2O_3+1,0\%CeO_2$	6,13	8,1	-	-	35,5 / 735	5,0	3,7

* second catalytic cycle

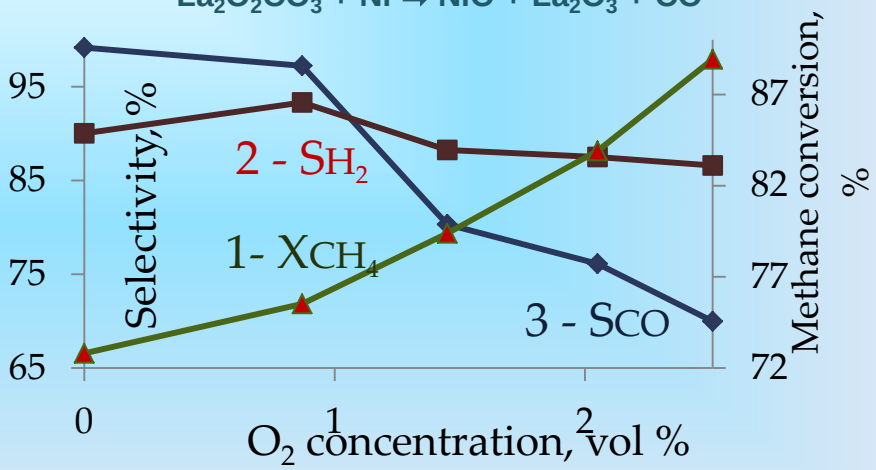
Oxygen effect in CDCM

on the activity and selectivity of the 6.3% Ni + 3.6% Al_2O_3 + 1.1% La_2O_3 catalyst :

1) methane conversion,
2) selectivity with respect to hydrogen,
3) selectivity with respect to carbon monoxide. Temperature 560° C

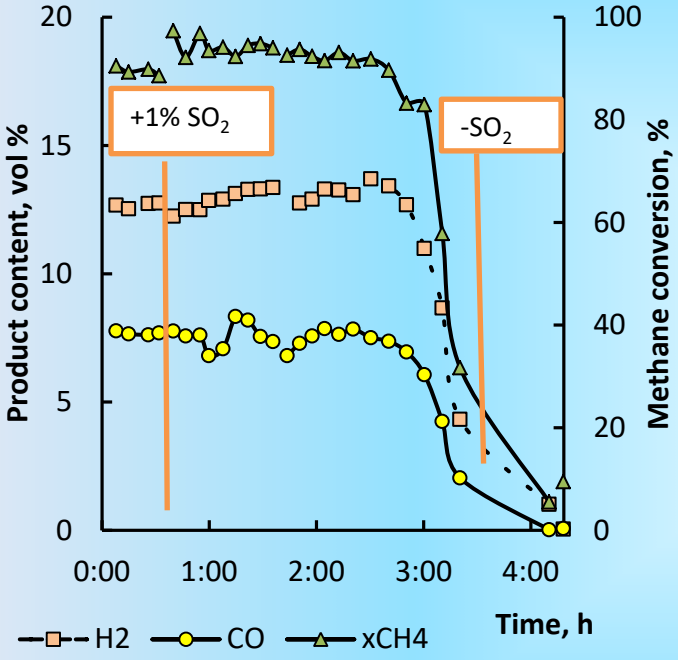
$La_2O_3 + CO_2 \leftrightarrows La_2O_2CO_3$

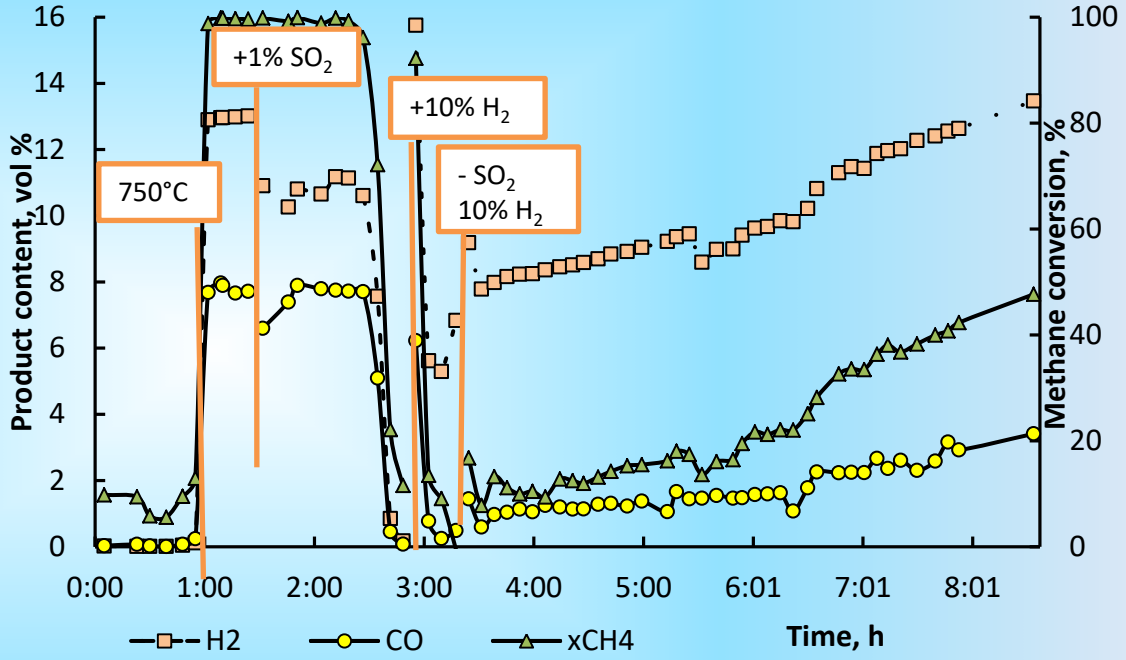
$La_2O_2CO_3 + Ni \leftrightarrows NiO + La_2O_3 + CO$



Changes in the indices of methane reforming process under the presence of sulfur dioxide (10000 ppm) and in the process of subsequent regeneration on the catalyst **$5\%NiO+4\%Al_2O_3+1\%CeO_2$**

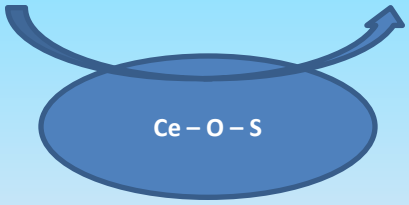
650°C, RM: 7,2% CH_4, 1,2%O_2, 2,8% CO_2, 2,8% H_2O. V_0 = 12000 h^{-1}.





$C_nH_m + H_2O$

$CO + H_2$

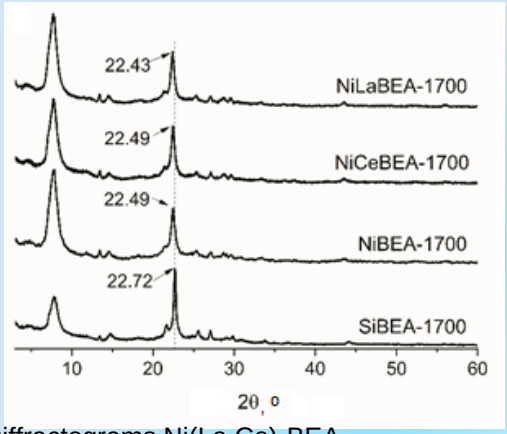


$SO_2 + H_2 = H_2S + H_2O$

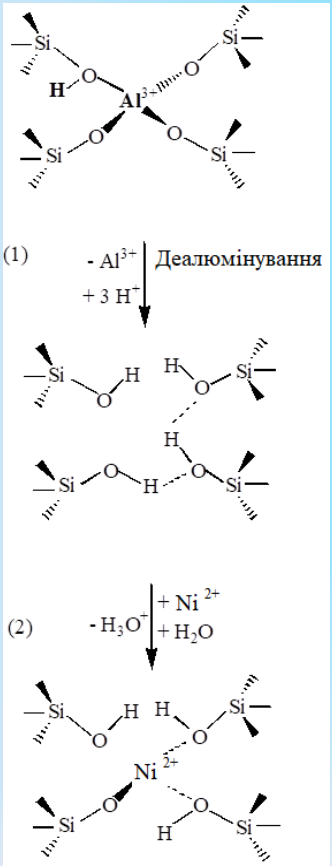
Ce-O-S + H_2 ⇨ H_2S

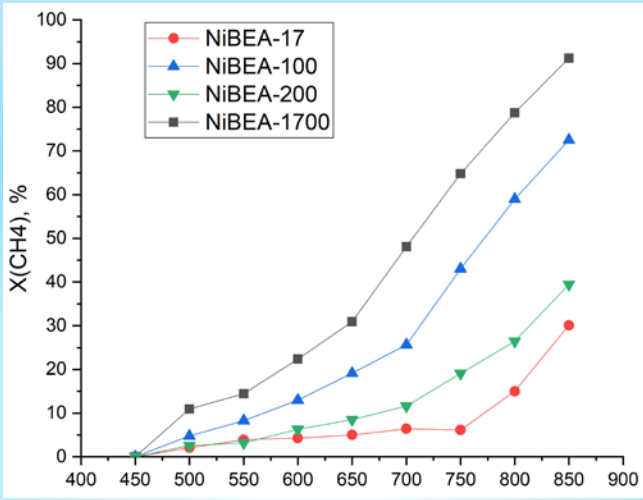
J. Catal. 2010 ***276*** *: 6 – 15*

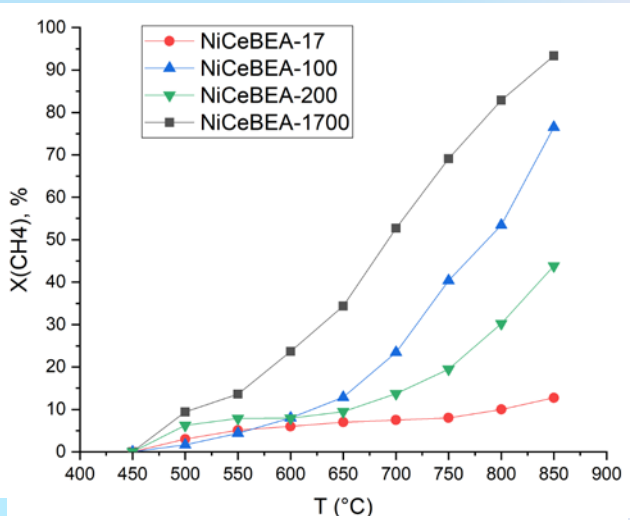
Carbon dioxide conversion of methane (CDCM) to hydrogen fuel (H_2 + CO) on Ni (La, Ce)-BEA zeolites

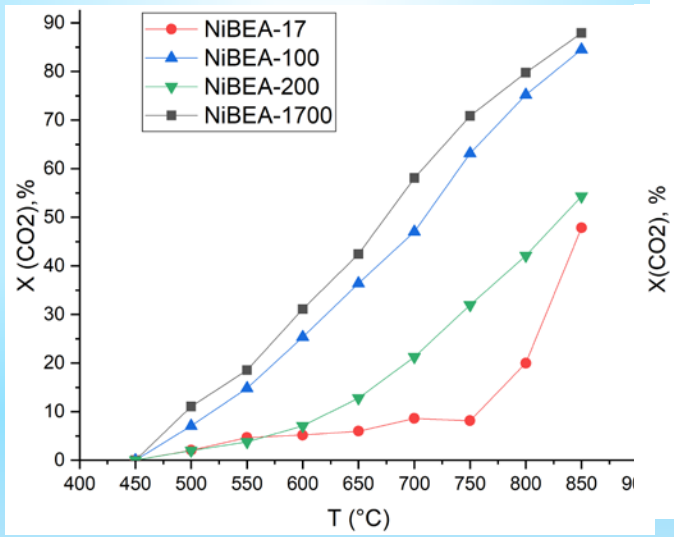


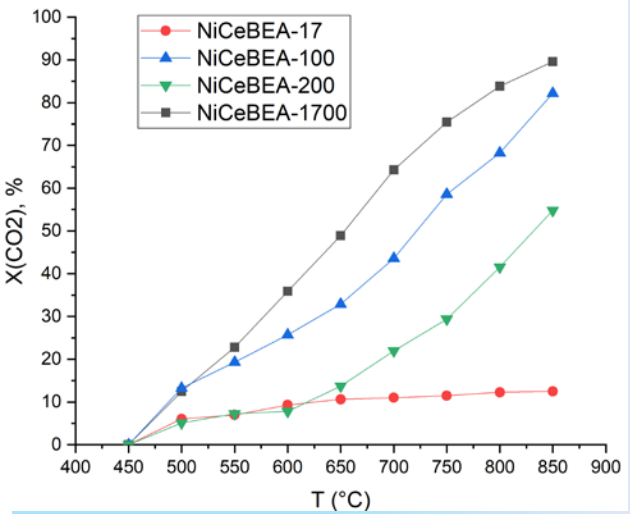
Diffractograms Ni(La,Ce)-BEA





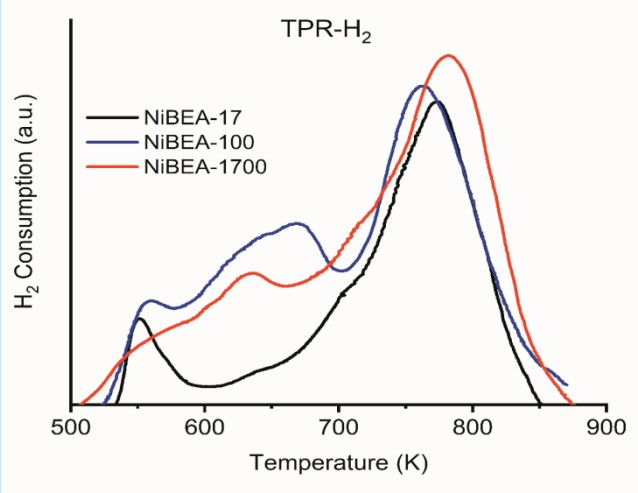




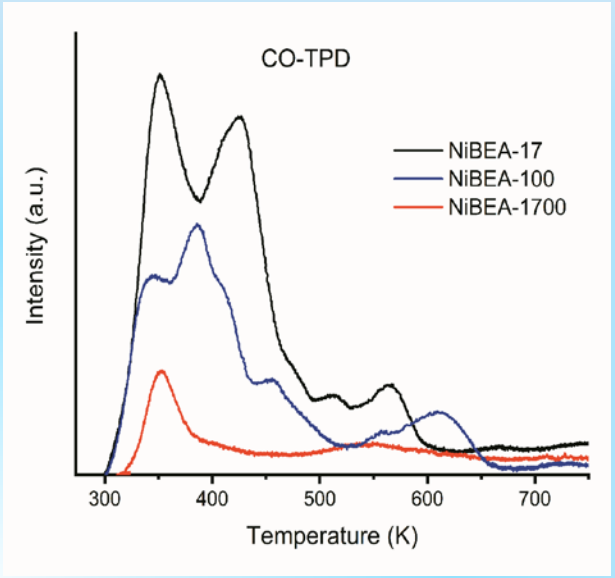


Conversion of 50% CH_4 + 50% CO_2 in the presence of NiBEA catalysts with different silicate modulus

Surface characteristics of Ni-BEA catalysts



H_2-TPR profiles for NiBEA catalysts with different Si/Al ratio



CO-TPD profiles for NiBEA catalysts with different Si/Al ratio

The proposed scheme of carbon dioxide conversion of methane on zeolite catalysts

$CO_2(ads.) + O^{2-} \leftrightarrow CO^{2-}_3(ads.)$
$CO^{2-}_3(ads.) + 2H_2(ads.) \leftrightarrow HCO^-_2(ads.) + OH^-$
$HCO^-_2 \leftrightarrow CO + OH^-$
$2OH^- \leftrightarrow H_2O + O^{2-}$
$C + O^{2-} \leftrightarrow CO^{2-}$

Additional stage of surface oxygen oxidation:
$C + H_2O \leftrightarrow CO + H_2$

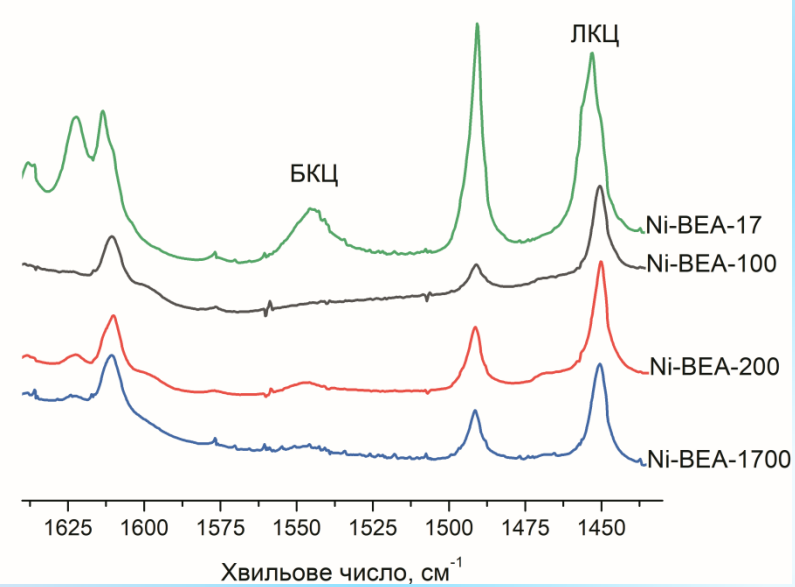
Total reaction:

$$CH_4 + CO_2 \leftrightarrow H_2O + CO + H_2$$

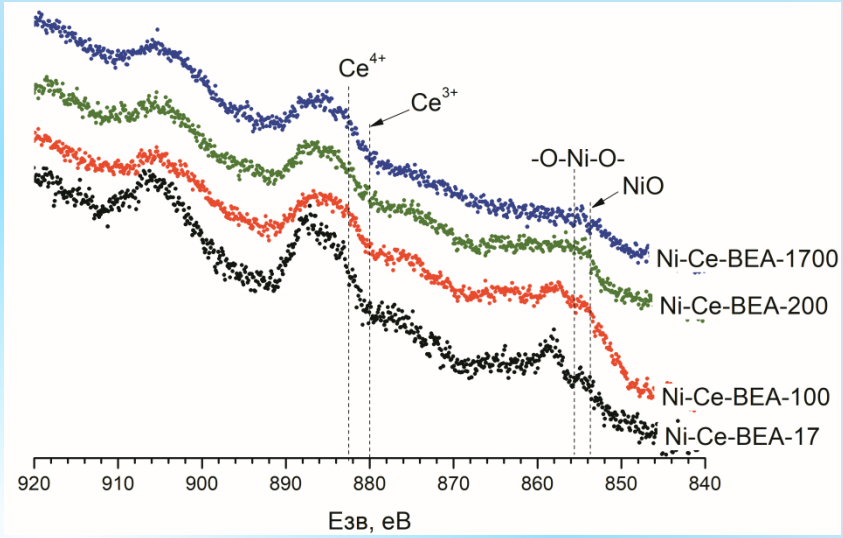
The main advantages of zeolite catalysts of the BEA type in the CDCM process:

- ***high activity;***
- ***the possibility of implementing the CDCM process without accumulating carbon;***
- ***the possibility of stable implementation of the CDCM process at stoichiometric ratios CH_4:CO_2***

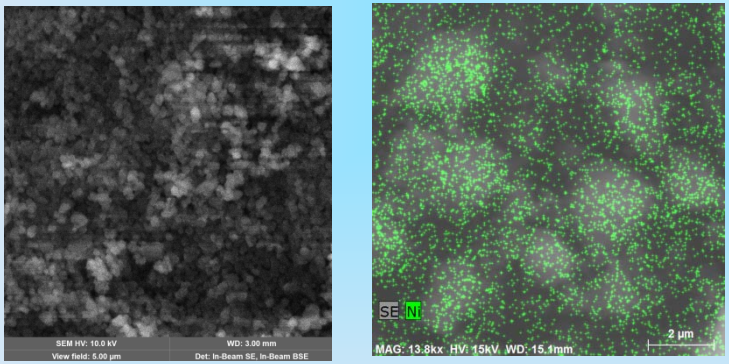
Structural and functional characteristics of Ni-BEA catalysts



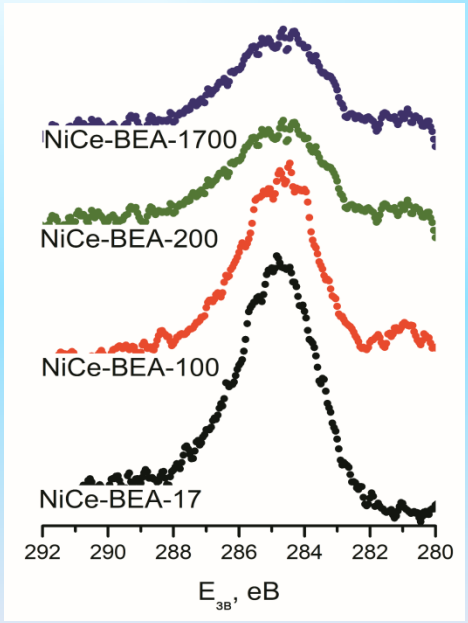
IR spectra of adsorbed pyridine on Ni-BEA catalysts after evacuation at 250 °C



XPS of Ni 2p and Ce 3d electrons of Ni-BEA samples



FESEM/EDX images of NiCe-BEA-1700 sample

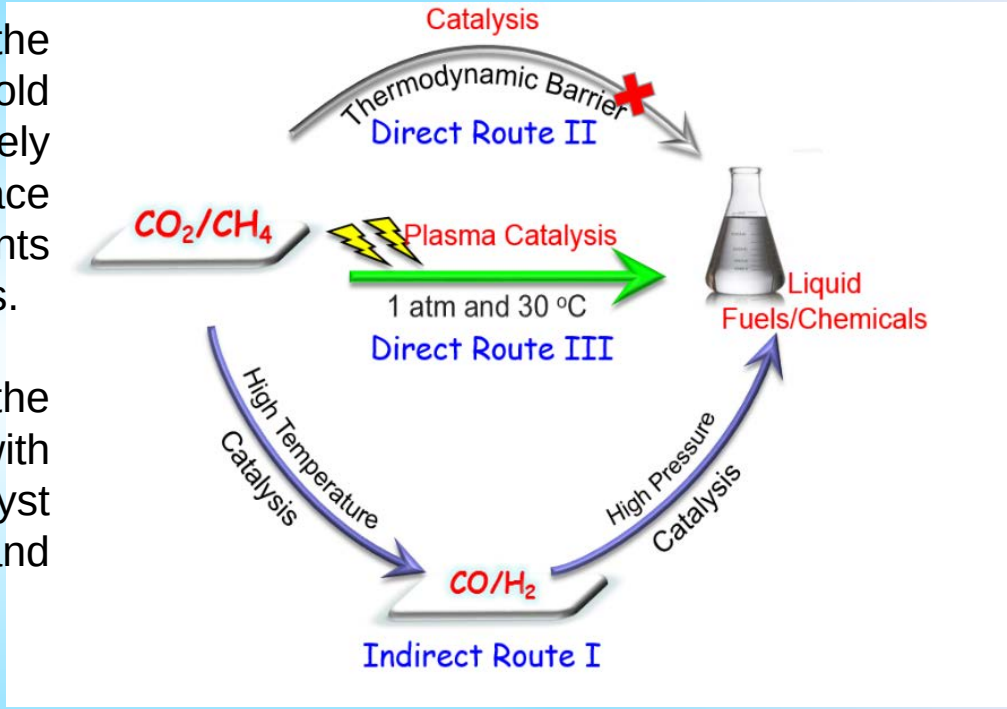


XPS of C 1s electrons of Ni-BEA samples after catalysis

Conversion of CH_4 + CO_2 to produce hydrogen, oxygenates and hydrocarbons in a plasma catalytic reactor

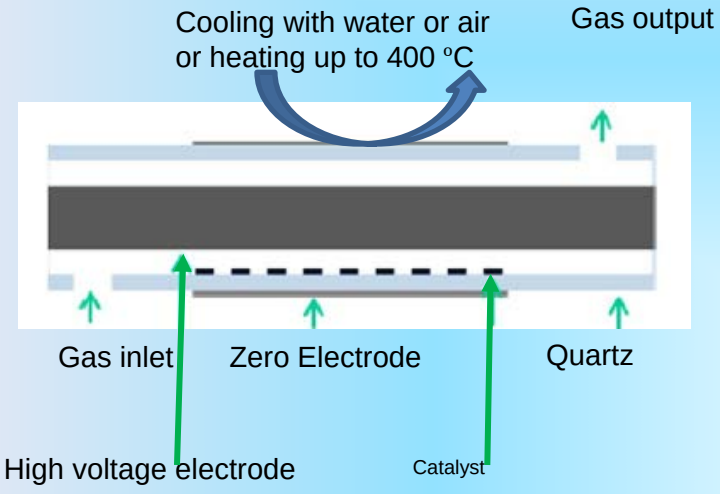
A promising way to involve carbon dioxide in the production process can be a combination of cold plasma, which will activate CO_2 at a relatively low temperature, and a catalyst, on the surface of which the interaction of activated reagents can occur with the formation of target products.

In general, the essence of plasmacatalysis is the generation of reactive particles in plasma with their subsequent interaction on the catalyst surface with the formation of hydrogen and valuable products.

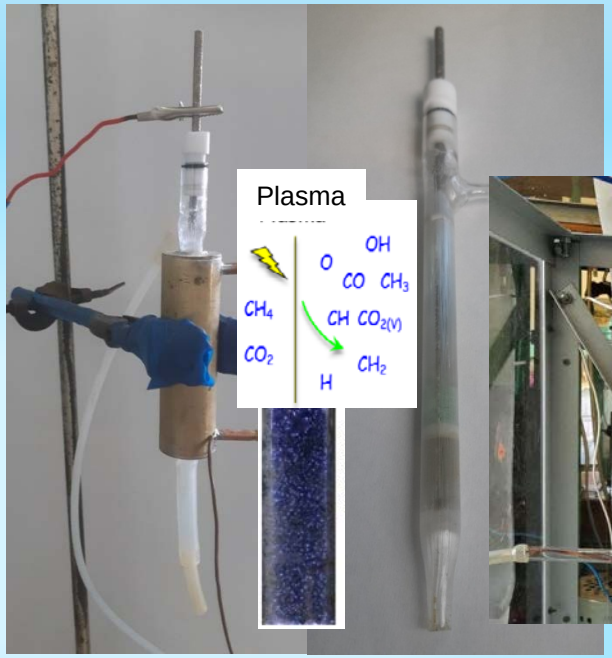


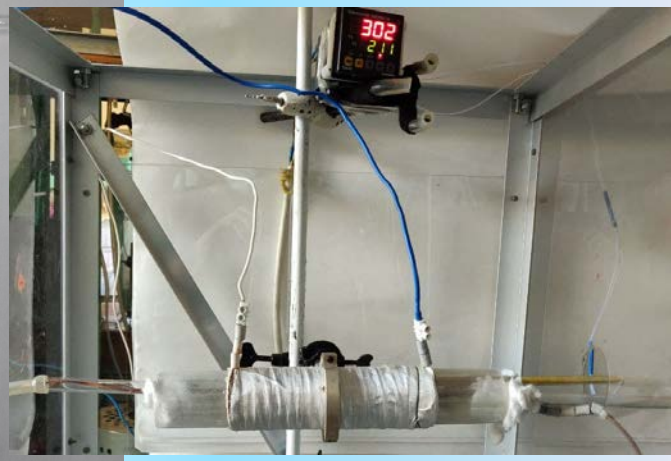
Wang et al. Angew. Chem. Int. Ed. 2017, 56, 13679 – 13683

Barrier discharge plasma catalytic reactor



Schematic diagram





Installations for plasma catalytic conversion of CO_2 and CH_4, constructed in department № 6 of the Institute of Physical Chemistry them. LV Pisarzhevskii NASU

The optimal design of the reactor for plasma catalytic conversion is a barrier discharge reactor (RBD).

This is due to a number of advantages:

•the possibility of activating the reactants with cold plasma, which allows you to place the catalyst directly in the reactor;

•no need to heat the reaction mixture due to the selective activation of molecules by plasma, which reduces energy consumption;

•scalability of the process - the results obtained in the laboratory reactor are commensurate with the industrial unit.

Plasmacatalytic conversion of CO_2 + CH_4 when the reactor walls are cooled to room temperature

Catalyst		Conversion,%		Selectivity,%				
		CH_4	CO_2	H_2	CO	C_nH_{2n+2}	C_nH_{2n}	$C_xH_yO_z$
10 W / 8,5 kHz / CH_4/CO_2= 1:1 (40 ml/min) / electrode - stainless steel								
ZnO/Al_2O_3		28	17	27	14	23	1	7
$CuO-ZnO/Al_2O_3$		25	16	51	10	21	1	11
$Ni-La/Al_2O_3$		27	17	50	14	19	1	5
Without catalyst	**stainless steel-electrode**	27	19	37	13	12	0	4
	Ni-electrode	24	16	53	14	14	0	5
	Cu-electrode	27	19	38	22	12	0	5
	Ti-electrode	25	19	34	23	12	0	5

- *The nature of the electrode and catalyst determines the selectivity of the plasmacatalytic process without substantial impact on conversion.*
- *Plasma catalytic conversion of biogas makes it possible to obtain not only hydrogen, but also valuable oxygenates, which can be used as a motor fuel.*
- *When the gas is converted in the range of 300-400 C, methane is converted with the preferred formation of hydrogen fuel. The presence of a catalyst in the discharge zone provides an increase in the conversion of the initial mixture.*

Without plasma, any conversion of reagents does not occur

Conclusions

- Modification of Ni-Al_2O_3/cordierite catalysts by rare earth metal oxides (La_2O_3, CeO_2) provides increase in their activity and operation stability in CDCM reaction.
- The introduction of oxygen into the reaction mixture has virtually no effect on the hydrogen selectivity of the CDCM process in the presence of the catalyst Ni-La_2O_3-Al_2O_3/cordierite and leads to a significant reduction (by 75-100^{0}C) in temperatures of achieving high conversions of methane.
- Poisoning of Ni-Al_2O_3/cordierite catalysts by sulfur compounds is caused by the presence of nickel in the Ni^0 state in their composition.
- Restoration of activity is possible by treatment of the pre-oxidized catalyst with hydrogen at high temperatures.
- It was found that zeolite catalysts Ni-BEA, prepared by postsynthetic introduction of Ni into the zeolite matrix, are characterized by high activity in the CDCM process.
- For the first time it was found that changing the value of the silicate modulus in the composition of Ni-BEA catalysts from 17 to 1700 increases their resistance to carbonization in the CDCM process by reducing the concentration of acid sites of the surface.
- It is determined that in the conditions of plasma-catalytic conversion of methane and carbon dioxide the optimal ratio of CO_2:CH_4 is 1:1, at which the highest yield of the target product (ethyl acetate) is observed. It is reasonable to assume that the reaction of formation of oxygenates occurs with the involvement of CO_2 in the process of C-C coupling.
- It was found that the nature of the electrode affects the conversion of reagents and the selectivity of the products formation; the highest conversion rates of reagents were achieved on copper and steel (grade 9XC) electrodes.

Publications based on research materials within the project

1. Orlyk, S.M., Kantserova, M.R., Chedryk, V.I., Kyriienko P.I., .Millot, Y., Dzwigaj, S. Influence of Acid–Base Surface Characteristics of GAxSIBEA Zeolites on their Catalytic Properties in the Process of Oxidative Dehydrogenation of Propane to Propylene with Participation of CO_2 Theoretical and Experimental Chemistry, 2021, 56(6), стр. 387–395 DOI 10.1007/s11237-021-09667-5

2. Космамбетова Г.Р., Трипольський А.І., Соловйов С.О., Стрижак П.Є., Каталізатори для автономних безполум'яних генераторів тепла. Збірка тез конференції з міжнародною участю «Функціональні матеріали для інноваційної енергетики», 13-15 травня 2019 р, Київ, с. 27.

Thank you for the attention!