OPTIMIZATION OF THE COMMERCIAL CATALYST FOR THE HYDROGENATION

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Introduction

**The most efficient industrial hydrocracking processes**

Firm developer	Temperature, °C	Pressure, MPa	Catalyst	Raw materials	The main product	Number stages
Isocracking Chevron	300-440	8.4	$NiS/Al_2O_3+SiO_2$	Heavy gas oil	Reactive fuel	One
Lomax UOP	310-430	10.0-15.0	$Co+Mo/Al_2O_3$ (HC115, HC215)	Light gas oil	Gasoline	Two
H-Oil	370-413	21.0	$Ni+Mo/Al_2O_3$	Heavy leftovers	Diesel fuel	One
H-Oil	430-445	25.0-30.0	Ni+Mo/zeolite	Heavy leftovers	Gasoline	Two
BASF	400-455	3.4-11.0	Ni+Mo/crystalline aluminosilicate	Light gas oil	Diesel fuel	One
BASF	420-450		Pd/zeolite type Y, for II degree	Vacuum distillates	Gasoline	Two
Leuna	320-390	4.0-8.0	$Ni+Mo/Al_2O_3+SiO_2$ (8207)	Vacuum distillates	Jet and diesel fuel	One
Leuna	320-390	4.0-30.0	$Ni+Mo/Al_2O_3+SiO_2$ (8213)	Heavy vacuum distillates	Diesel fuel, base oils	One

To date, with the existence of a significant number of modifications of catalysts that are successfully used in the oil refining industry, it is the process of hydrocracking has not received mass introduction. This is associated with significant capital and operating costs for this process. This is due to harsh conditions to ensure stable operation of the catalyst (minimum temperature - 350 ° C, minimum effective hydrogen pressure of 10.0 MPa).

Hydrocracking conditions can be mitigated by maintaining the efficiency of the process by replacing existing granular catalysts with membrane ones. The main advantage of membrane catalysts over granular is the maximum use of the active surface, which primarily allows eliminating diffusion inhibitions in the supply of reagents and removal of products. In addition, the use of membrane catalysts allows, in addition to temperature and pressure, to use other levers of influence on the active centres of the catalyst. For example, one such lever may be a directed flow of protons.

Given our previous experience in controlling the activity of the catalyst, the application of proton current at the bifunctional contact creates the possibility of influencing both the acid-base centres and the redox. At acid centres, you can control a certain amount of water formed, which affects the mobility of the proton in the active centre. Conditions for facilitated formation of active hydrogen in the atomic state are created at redox centres. Thus, just the combination of the membrane catalyst with the directed flow of protons through it allows mitigating the conditions of hydrogenation processes.

Experimental
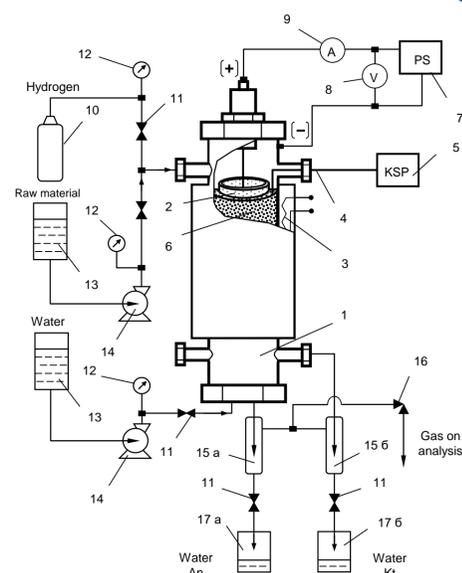
Scheme of catalytic laboratory installation: 1 – membrane reactor; 2 – membrane; 3 – electric heater; 4 – thermocouple; 5 – the device registering KSP-4; 6 – graphite current contact jaw; 7 – DC power supply; 8 – voltmeter; 9 – ammeter; 10 – hydrogen cylinder; 11 – valve; 12 – manometer; 13 – measuring capacity; 14 – plunger pump; 15 – separator; 16 – pressure regulator; 17 – prefabricated capacity.

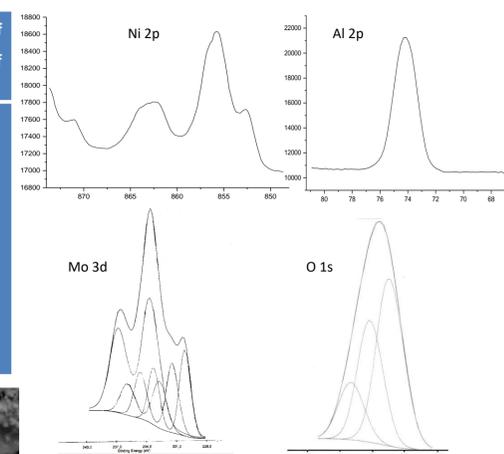## Results and discussion

Proton conducting polymers (DHPCA)
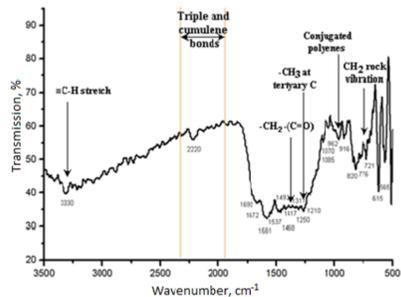
Element content, %, mas.			
C	H	N	Residual (incl. O)
70.82	4.98	0.95	23.25
72.16	4.78	0.87	22.19
Molar ratio C / H	2.36		2.54
Molar ratio C / H / O	5.9/2.5/1.0		6/2.4/1
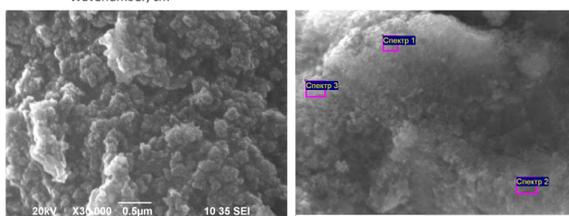
Element	Content, %		
	Spectrum 1	Spectrum 2	Spectrum 3
C K	81.08	81.35	80.10
O K	17.21	16.82	18.21
Cl K	1.50	1.53	1.33
Ca K	0.21	0.30	0.21
Cu K			0.15
Total:	100	100	100

Catalyst

| Electron level	E b., eV	Compound	Reference data	Elements content, %, at.	The composition of the surface layer of the catalyst
Ni $2p_{3/2}$	852.6	Ni	852.6	2.9	
	855.8	$NiMoO_4$	856.0		
Mo $3d_{5/2}$	229.3	MoO_2	229.2	14.2	$Ni_{2.9}Mo_{14.2}$ $Al_{12.7}O_{70.2}$
	230.6	Mo_4O_{11}	230.8		
	231.9	$NiMoO_4$	231.9		
	232.8	MoO_3	232.6		
Al $2p_{3/2}$	74.3	$\gamma-Al_2O_3$	74.2	12.7	
O $1s_{1/2}$	531.6	$\gamma-Al_2O_3$	531.6	70.2	
		MoO_3	531.9		

Spectrum	Element content on the surface, %, mass.			
	O	Al	Ni	Mo
1	32.66	3.19	1.57	62.58
2	27.15	2.27	1.08	69.49
3	29.51	3.15	1.02	66.32
4	27.44	0.63	0.75	71.18
5	36.98	8.39	3.07	51.55
6	36.91	11.77	5.07	46.26
7	30.43	4.13	2.05	63.38
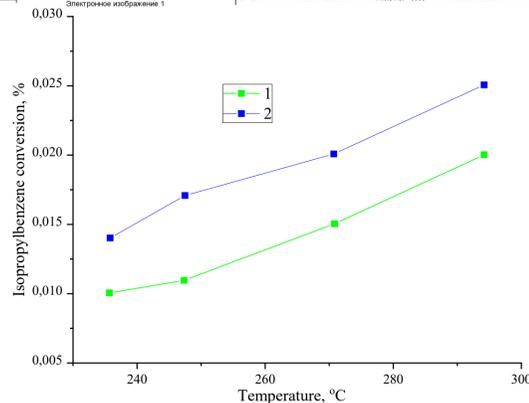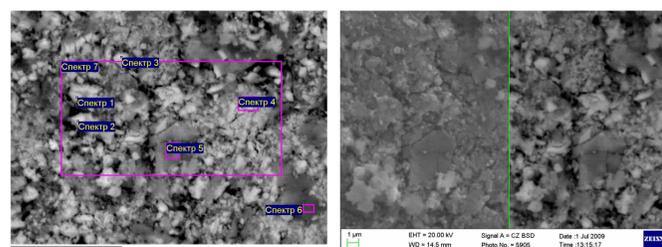
Temperature dependence of isopropylbenzene conversion on granular (1) and membrane (2) catalysts
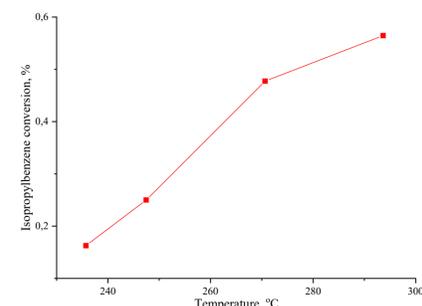
Temperature dependence of isopropylbenzene conversion on a composite membrane catalyst containing DHPCA at a proton flux intensity of 0.05 A and a pressure of 4.0 MPa

Conclusion

An analogue of an industrial aluminum-nickel-molybdenum (ANM) catalyst was synthesized: 8–10% NiO, 15–20% MoO_3, 70–77% Al_2O_3. The reduced catalyst contains on the surface of the particles of metallic nickel and molybdate nickel $NiMoO_4$ with the elemental composition of the catalyst layer to a depth of 5 nm $Ni_{2.9}Mo_{14.2}Al_{12.7}O_{70.2}$. A method for producing proton-conducting membranes on an elastic basis and a composite membrane catalyst based on porous ceramics sintered from aluminum and zirconium oxides at 1400 °C has been developed. The pores of the membrane carrier are filled with proton-conducting material (10–20% wt.) Followed by application to the inner and outer surfaces of the ANM catalyst (80–90% wt.). When creating a directed flow of protons through the membrane catalyst on its surface in the reaction zone, hydrogen radicals are generated, as a result of which the activity of the catalyst 10–12 times increases.