

Maxim Popov^{1, 2}, Andrey Zagoruiko³, Andrey Brester², Sergey Lopatin³

¹N.D. Zelinsky Institute of Organic Chemistry Russian Academy of Sciences, Moscow, Russia

²Novosibirsk State Technical University, Novosibirsk, Russia

³Boreskov Institute of Catalysis, Novosibirsk, Russia

PP-24

INTRODUCTION

Carbon nanofibers (CNFs) are a modern gas processing product due to their high strength, chemical purity, chemical inertness and developed surface. CNF can be used as a carbide-forming agent for the synthesis of refractory materials (TiC, B₄C, Cr₃C₂, VC, etc.), can be used as a catalyst for the selective oxidation of hydrogen sulfide to sulfur. Carbon nanofibers have great prospects for use as a carrier for a metal catalyst, as well as a sorption carbon material for gas sensors.

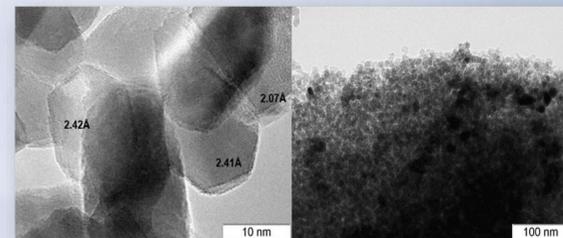
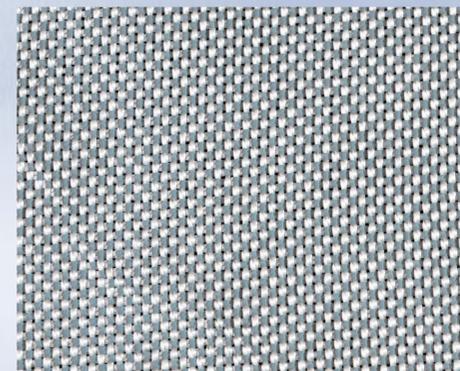
The glass microfiber fabric, characterized with high uniform structure, flexibility, mechanical and thermal stability, is the promising support for creation of various catalytically active systems. The current study was dedicated to the deposition of carbon nanofibers (CNF) at the glass fiber support modified with additional layers of silica and nickel oxide.

CATALYSTS SYNTHESIS

- The high-silica glass-fiber fabric (GFF) KT-11-TO (produced by Stekloplastik Co., Zelenograd, Russia), was used as the primary GFC support (thermal stability limit as high as 1100C).
- As the secondary support, we used SiO₂ (~15%), which has the thermal expansion coefficient close to that of primary glass.
- The unit surface area of the support increased from 0.5 m²/g (for initial GFF) up to 20-30 m²/g.
- The unit pore volume was increased from 0.0005 to 0.03-0.04 cm³/g; the average pore diameter was equal to 6.5- 6.7 nm.
- The modified GFF was impregnated by the water solution of nickel acetate.
- After the impregnation and drying, the catalyst samples were thermally treated using the surface thermo-synthesis method by heating from ambient temperature up to 500C.

CATALYSTS PROPERTIES

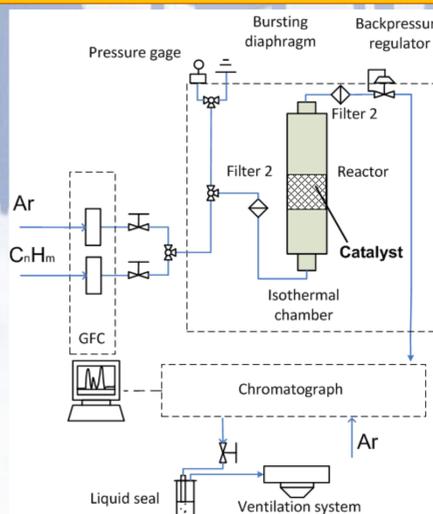
- Ni content in the catalyst – 2.0% mass (for metal Ni)
- Specific surface area – 12 m²/g
- Pore volume 0.03 cm³/g, average pore diameter ~8 nm
- Ni state (according to XRD data) – β-NiO phase (structural type NaCl, space group *Fm3m*) with the average crystallite size calculated by Scherrer formula 12–17 nm
- NiO state (according to TEM data) – large porous agglomerates (45-700 nm) of particles 15 -25 nm, with inclusion of NiO particles of 3-5 nm in the bulk of SiO₂ layer



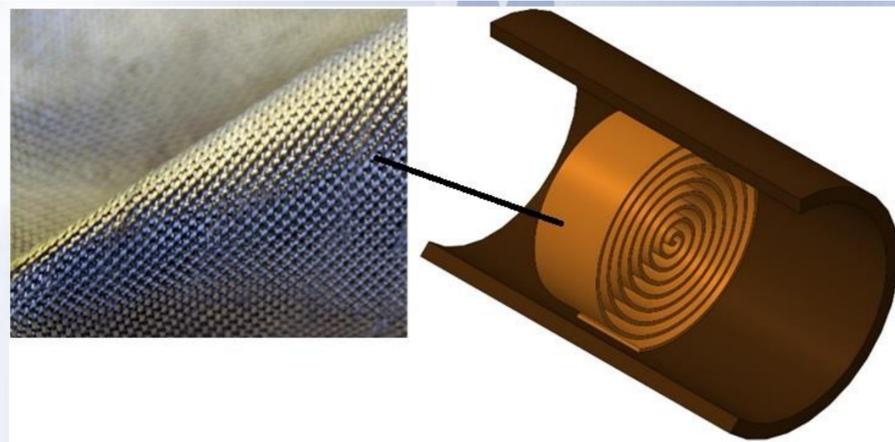
CATALYTIC DECOMPOSITION OF LIGHT HYDROCARBONS

The experiments were carried in the Autoclave Engineers BTRS-In setup in a metal tubular reactor at a temperature of 550-600°C, pressure was 1–2 bar.

Gases were used: APG, vol.% (CH₄ - 85%, C₃H₈ - 11%, C₄H₁₀ - 3%, C₂H₆ - 1%, H₂S <0.003%) and pure methane (CH₄ - 99.999%) in the process of catalytic decomposition.



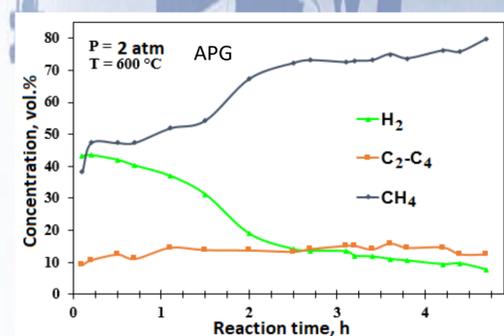
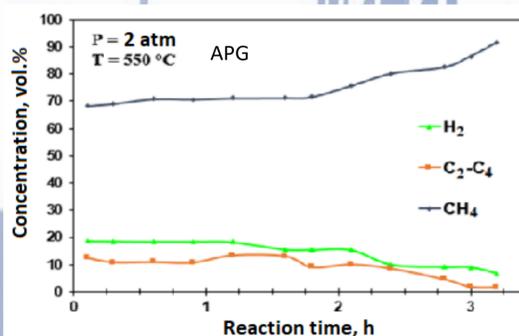
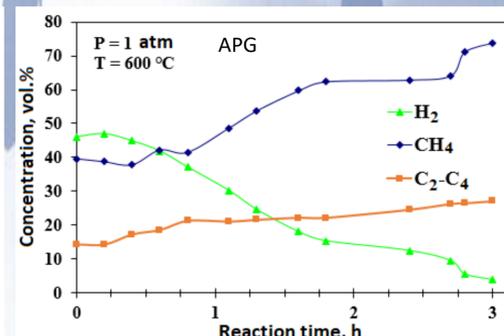
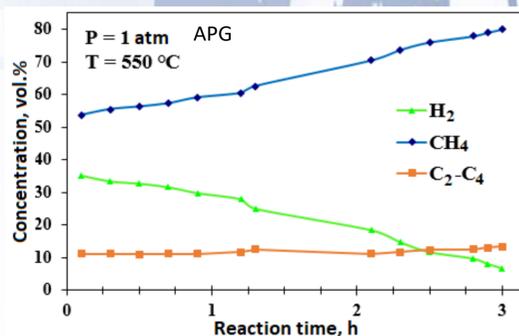
The catalyst was twisted into a spiral and placed in a flow-through metal reactor



RESULTS

The table shows the data rate of formation of hydrogen and carbon nanofibers depending on various process conditions

T, °C	Hydrogen production rate, l/min·g _{cat}		CNF formation rate, g/min·g _{cat}	
	CH ₄	APG	CH ₄	APG
Pressure: 1 bar				
550	0.75	0.92	0.0047	0.0038
600	1.0	1.1	0.0029	0.0050
Pressure: 2 bar				
550	0.75	0.57	0.0032	0.0043
600	1.1	0.81	0.0047	0.0051



CONCLUSIONS

It was determined that with increasing temperature of the process of catalytic decomposition of the initial hydrocarbon on a glass-fiber catalyst the specific rate of hydrogen formation increases. At the same time, with increasing temperature catalyst lifetime decreases, regardless of the initial hydrocarbon used. With an increase in pressure from 1 to 2 bar a significant increase in the catalyst lifetime occurs regardless of the initial hydrocarbon used. It was found that during the catalytic decomposition of APG the rate of hydrogen formation decreases by 16% at 550 °C and by 29% at 600 °C with an increase in pressure from 1 to 2 bar.

Thus, the use of glass-fiber catalysts with low nickel content may be promising for catalytic decomposition of hydrocarbons with formation of hydrogen without carbon emissions to atmosphere. In case of APG processing on the base of the proposed approach it is possible to use the produced hydrogen for primary hydroprocessing of the produced oil to decrease its sulfur content and viscosity before transportation. The co-produced nano-fibrous carbon may be used as a sorbent to prevent the pollution of environment by hydrocarbons.

IV Scientific-Technological Symposium



CATALYTIC HYDROPROCESSING IN OIL REFINING

APRIL 26 - 30 2021 / ONLINE

