EFFECT OF THE MODIFYING RUTHENIUM ADDITIVE ON THE STRUCTURE AND ACTIVITY OF IRON-CONTAINING CATALYSTS

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FISCHER-TROPSCH SYNTHESIS REACTIONS

✓ Main :

Alkanes $nCO + (2n+1)H_2 \rightarrow C_nH_{2n+2} + nH_2O$

Alkenes $nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O$

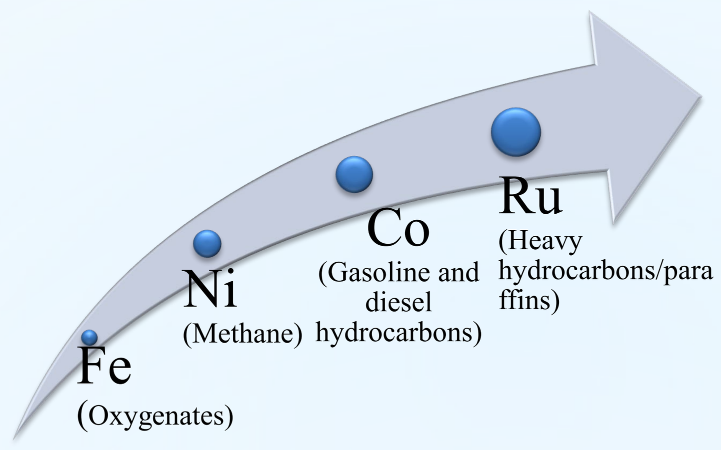
Water gas shift $CO + H_2O \rightarrow CO_2 + H_2$

✓ Side reactions:

Alcohols $nCO + 2nH_2 \rightarrow H\text{-}(CH_2\text{-})OH + n\text{-}1H_2O$

Boudoir Reaction $2CO \rightarrow C + CO_2$

FISCHER-TROPSCH SYNTHESIS CATALYSTS

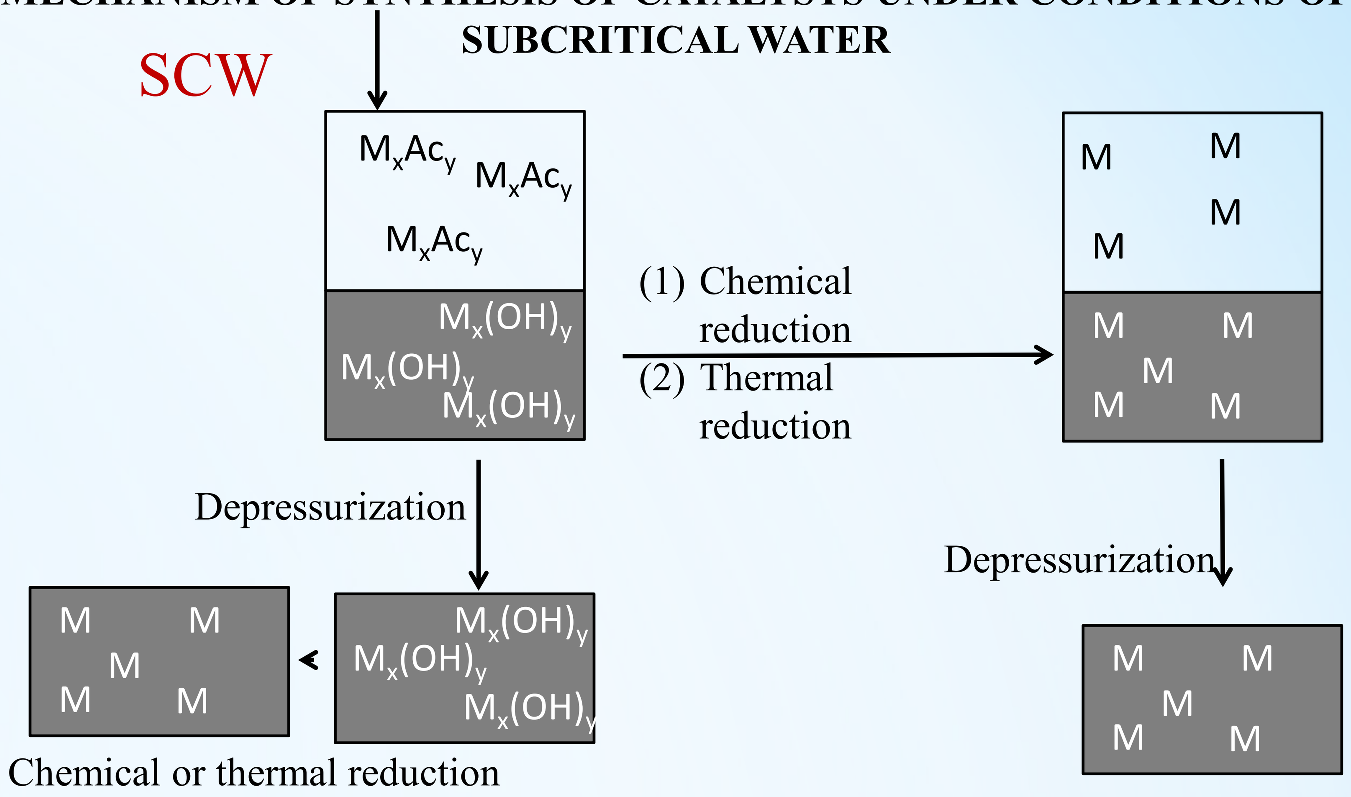


✓The action of the metal-catalyst in the Fischer-Tropsch synthesis depends on the nature and mechanism of adsorption of synthesis gas on the surface.

✓Transition metals with 3*d* and 4*f* electrons are the most suitable for dissociative adsorption of CO and H_2.

✓The highest catalytic activity is shown by Ru, Co, Ni and Fe.

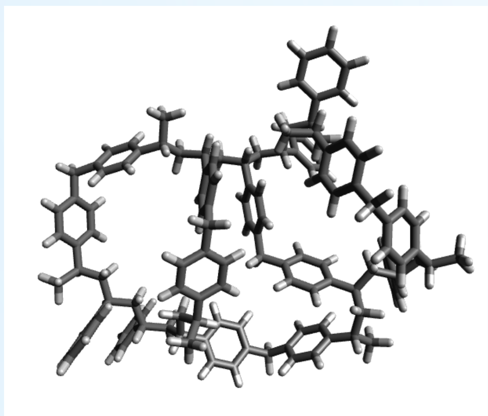
MECHANISM OF SYNTHESIS OF CATALYSTS UNDER CONDITIONS OF SUBCRITICAL WATER

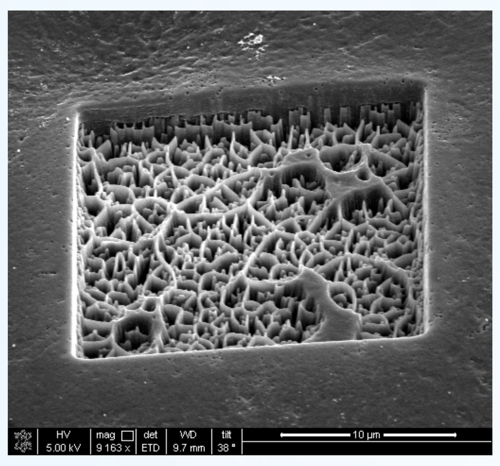


THE USE OF HYPERCROSSLINKED POLYSTYRENE (HPS) AS A SUPPORT FOR CATALYST SYNTHESIS

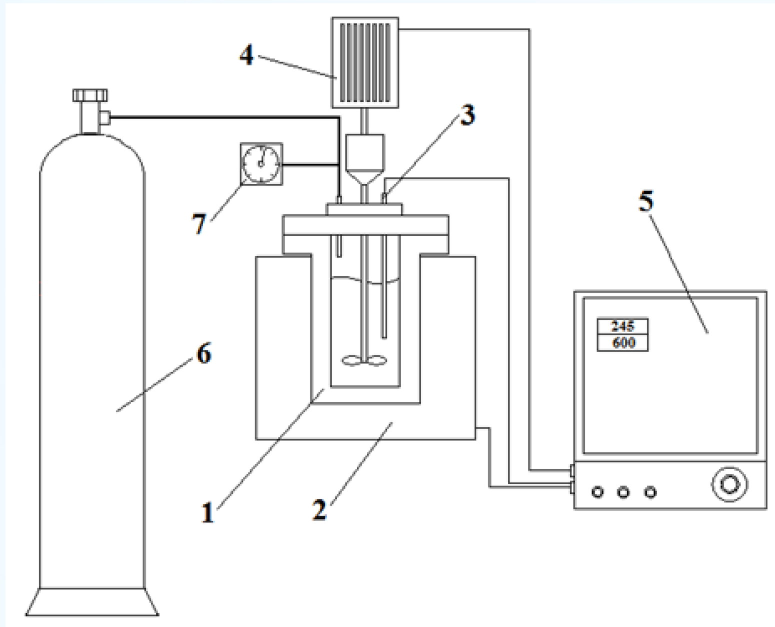
It has several advantages:

- ✓ High surface area (up to 1500 m^2/g).
- ✓ Presence of mesopores facilitating transport of reacting molecules to and from the active sites.
- ✓ Chemical inertness.
- ✓ Possibility to use for fixed bed applications.
- ✓ Thermal stability (up to 450 °C).





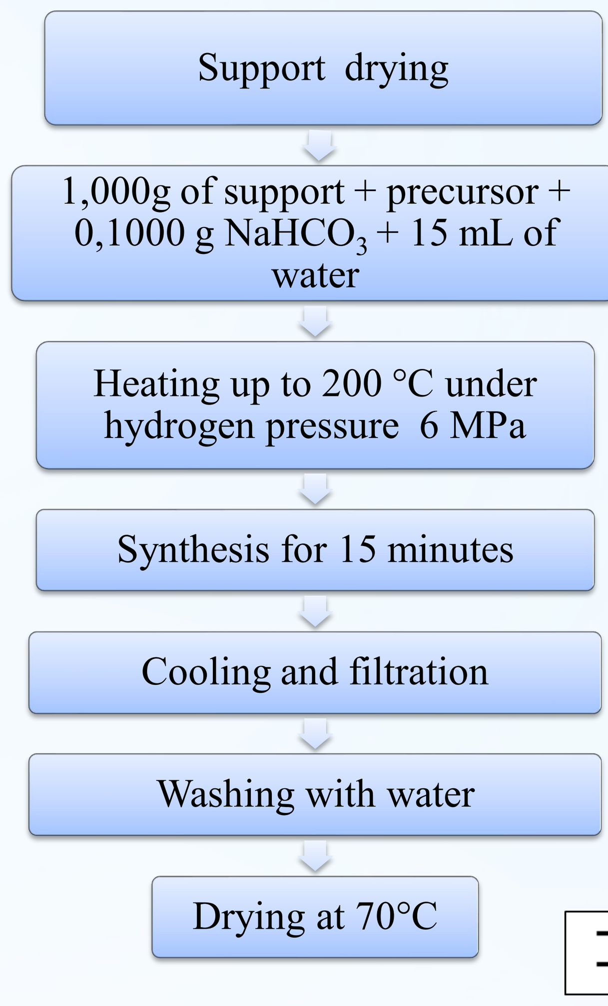
SYNTHESIS TECHNIQUE



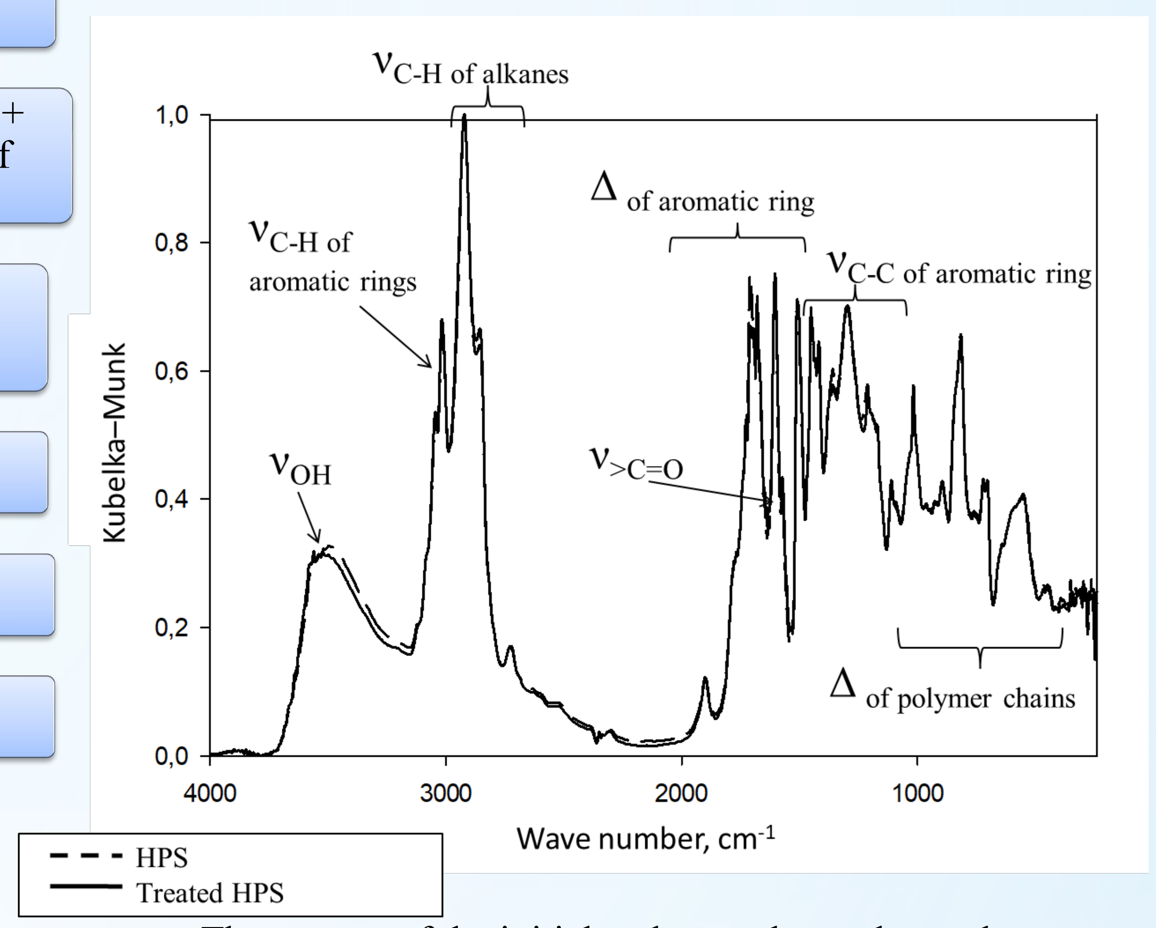
Laboratory setup for catalyst synthesis includes high-pressure reactor (1), heater (2), thermocouple (3), stirrer motor (4), control unit (5), nitrogen bottle (6), and manometer (7).

Following catalysts were prepared by this way :

- 10%-Fe-HPS
- 10%Fe-1%Ru-HPS
- 2%Fe-1%Ru-HPS



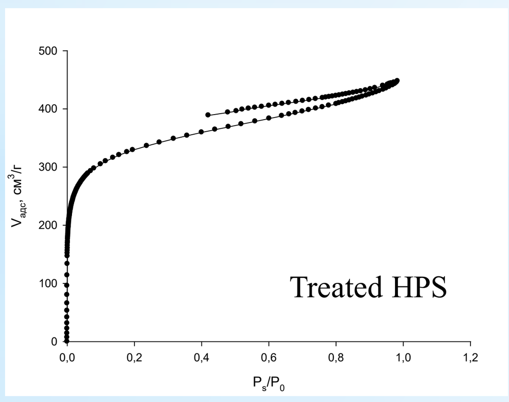
STABILITY OF THE SUPPORT DURING THE SYNTHESIS OF CATALYSTS

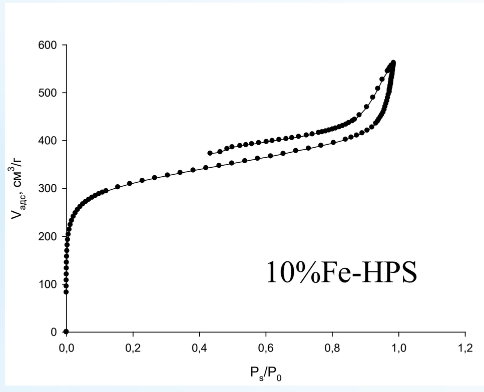


The spectra of the initial and treated samples under synthesis conditions practically do not differ

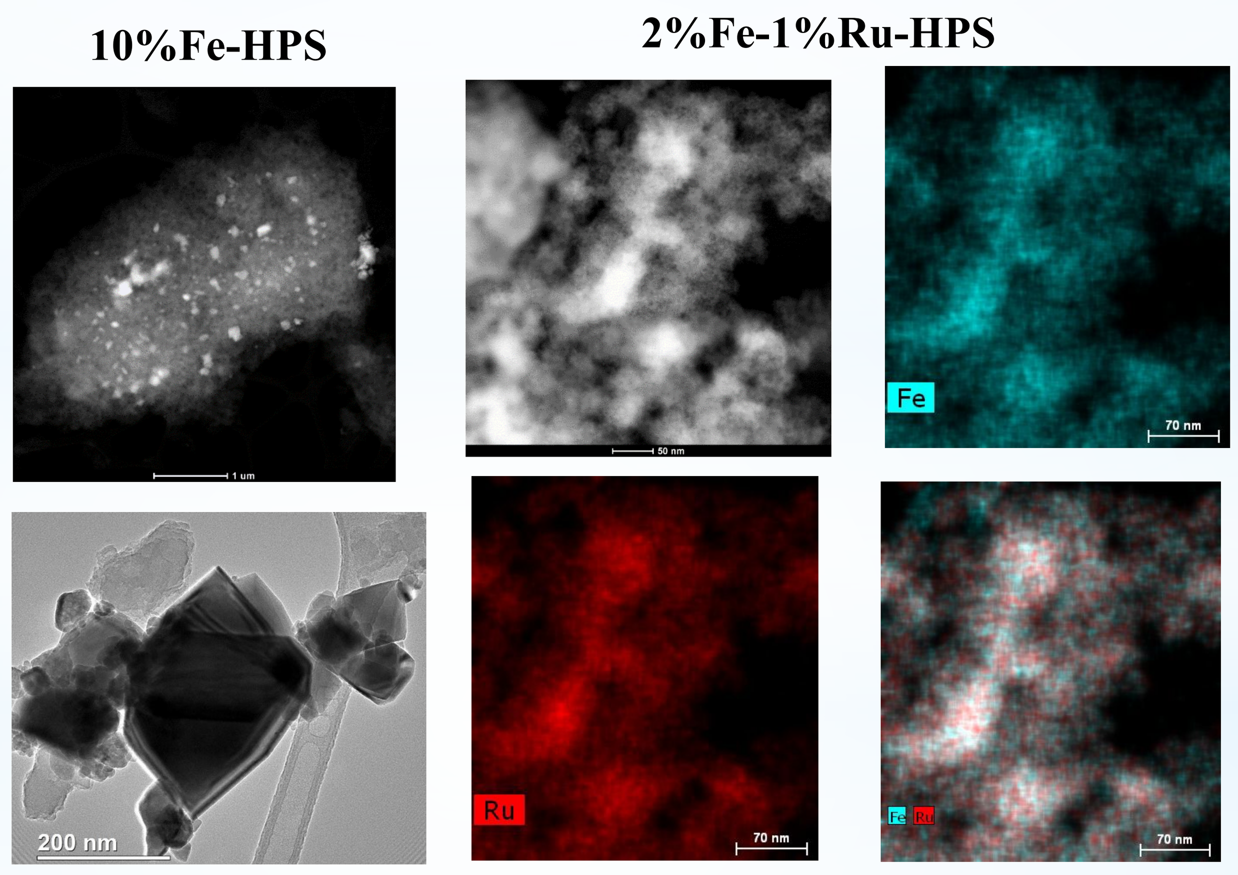
LOW-TEMPERATURE NITROGEN ADSORPTION

Sample	Total pore volume V_p, cm^3/g	Specific surface area			
		Langmuir Model S_L, m^2/g	BET Model S_{BET}, m^2/g	t-plot S_t, m^2/g mesopore	micropore
Treated HPS	0,70	1276	1276	247	915
10%Fe-HPS	0,89	1178	1048	236	805
10%Fe-Ru- HPS	0,89	1217	1091	263	821

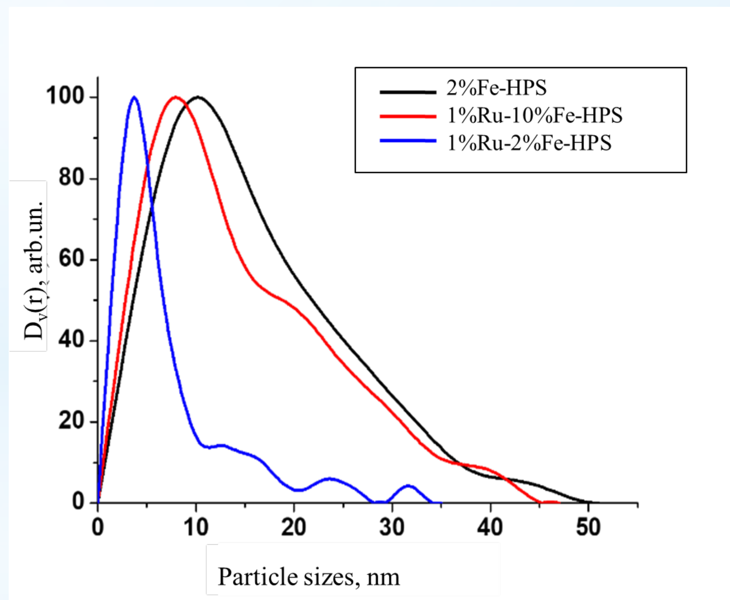




HRT AND ELEMENT MAPPING

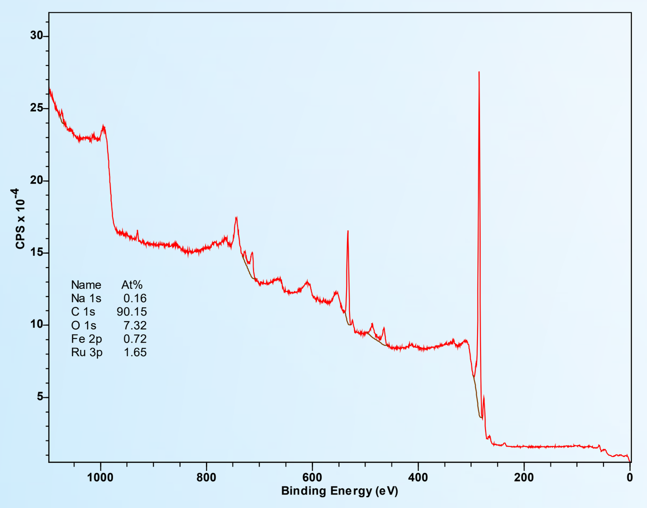


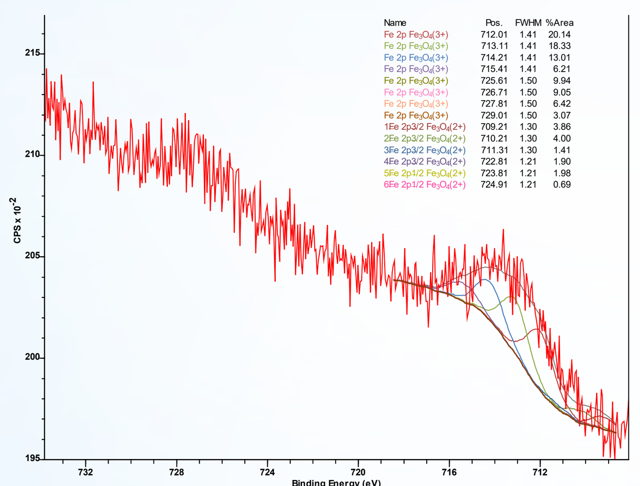
SMALL-ANGLE X-RAY SCATTERING

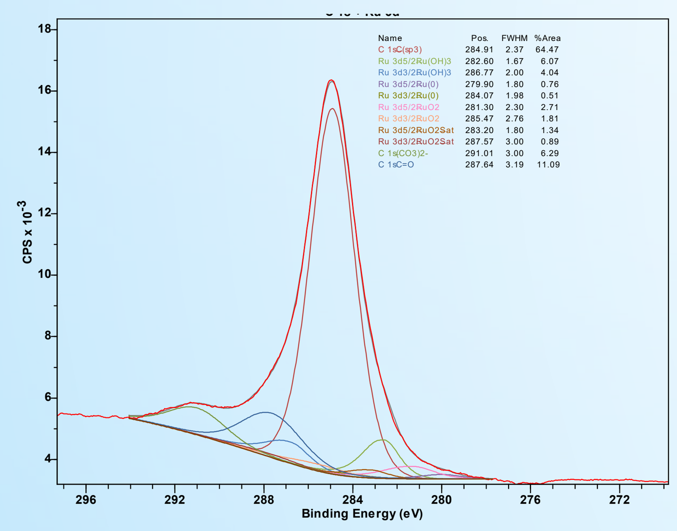


Sample	D, nm
2%Fe-HPS	20-40
1%Ru-2%Fe-HPS	3-7
1%Ru-10%Fe-HPS	15-30

X-RAY PHOTOELECTRON SPECTROSCOPY







According to mathematical modeling data, the active phase is represented by:

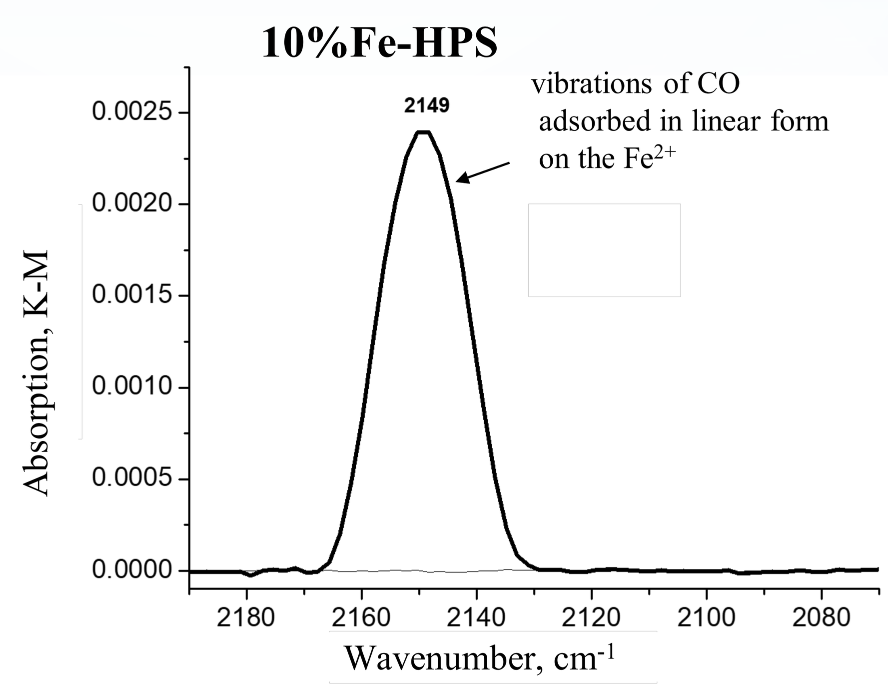
✓ Fe_3O_4;

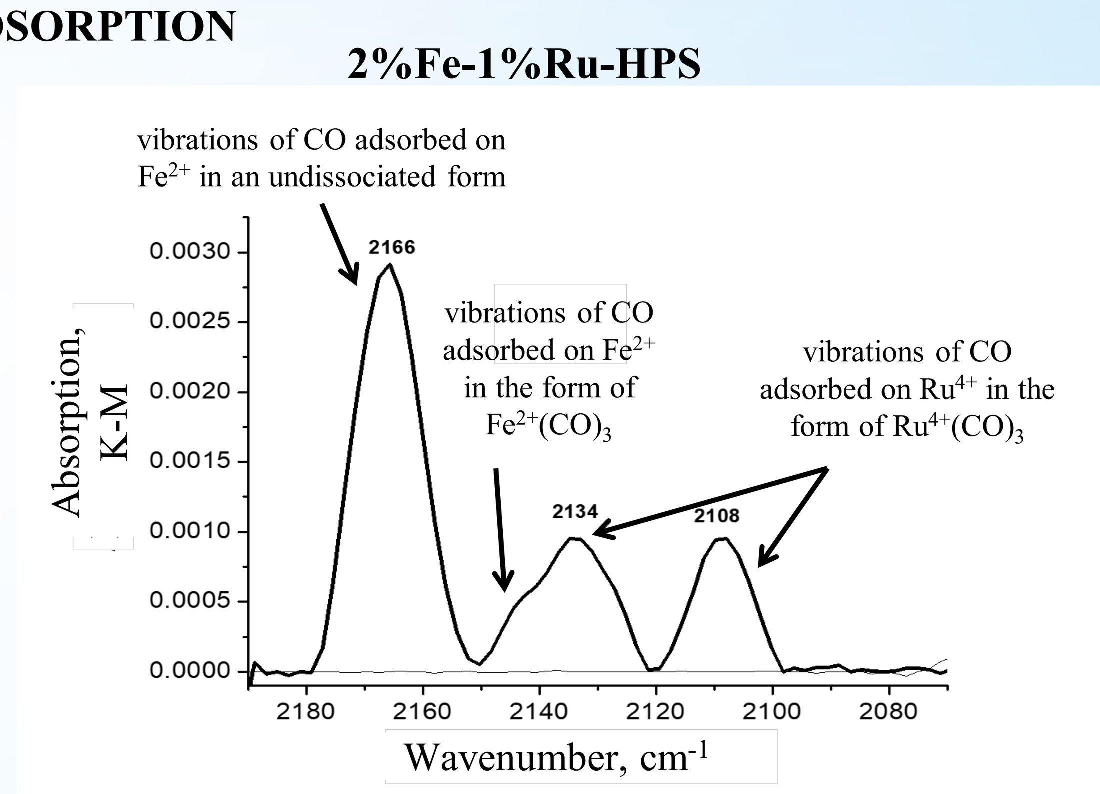
✓Ru;

✓$Ru(OH)_4$;

✓RuO_2

INFRARED SPECTROSCOPY OF DIFFUSE REFLECTION OF CO ADSORPTION





CONCLUSIONS

The characteristics of ruthenium-doped iron catalyst synthesized by subcritical deposition were studied. Analysis of the obtained samples showed that the synthesized catalysts have a mesoporous structure with a high specific surface area and a uniform distribution of the active phase. The use of subcritical conditions during the application of the active phase does not lead to destruction in the structure of the polymeric support. The proposed catalysts exhibit high activity and stability in the process of liquid-phase FTS.

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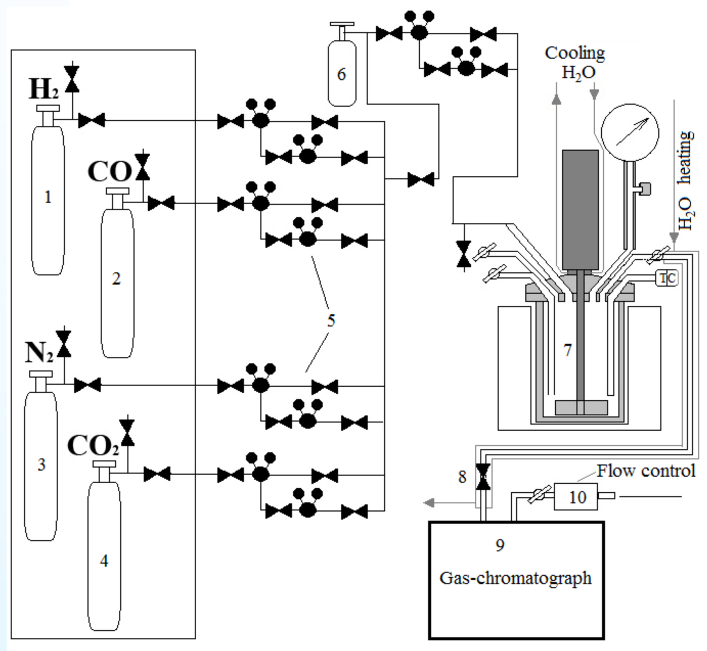
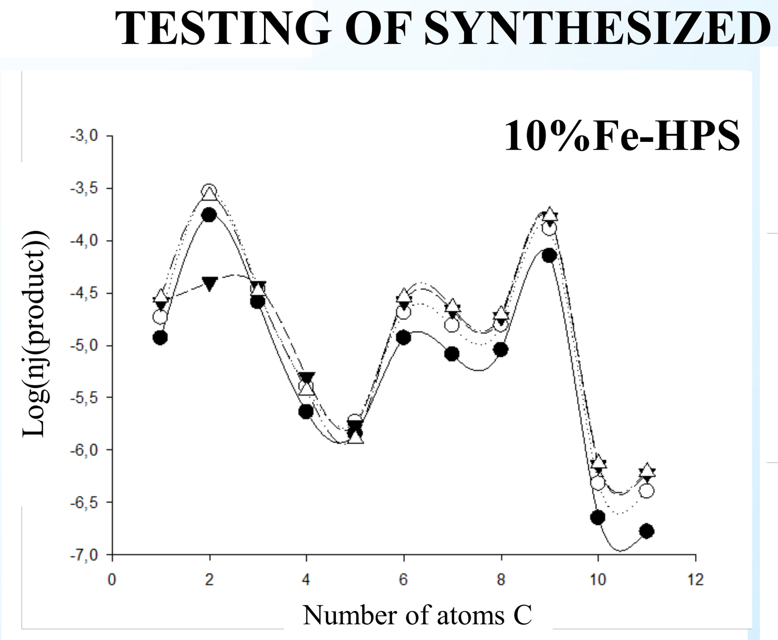
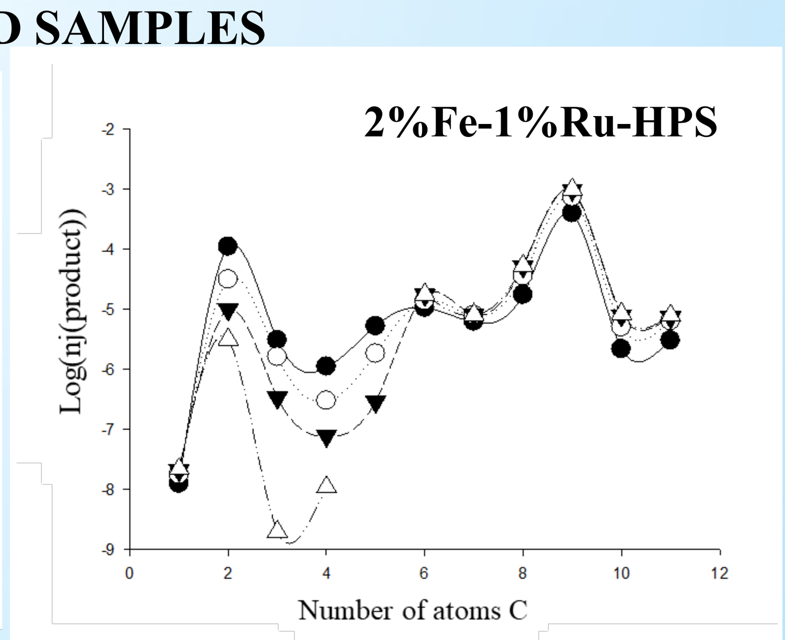
TESTING OF SYNTHESIZED SAMPLES



- ✓Catalyst mass– 0.1000 g
- ✓Solvent (Dodecane) vol– 10,0 ml
- ✓ Temperature – 200 °C
- ✓Stirring rate– 750 rpm
- ✓$CO:H_2$ = 1:4 (Vol.)
- ✓Synthesis gas pressure– 2.0 MPa





Catalyst	Conversion CO*, mol. %	Selectivity**, mol. %			
		C_1-C_4	C_5-C_{11}	Oxygenates C_2-C_4	Olefins C_5-C_6
10%Fe-HPS	24,5	9,5	71,7	15,8	2,2
2%Fe-1%Ru-HPS	29,8	1,0	98,5	0,2	0,3