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Novel polyacrylonitrile-based C/Co-Ru metal-carbon nanocomposites as effective catalysts for ethanol steam reforming

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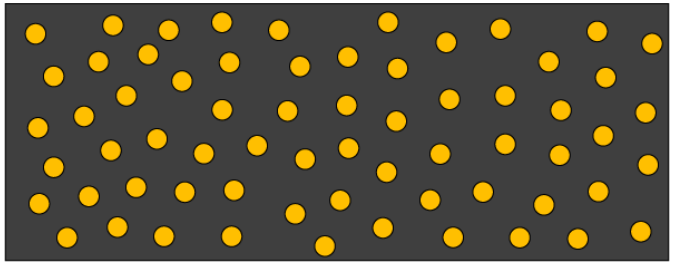
Metal-carbon nanocomposites

Materials consisting of metal nanoparticles distributed on supports of different nature are promising due to multifunctional properties useful in a wide range of commercial and scientific applications

Supports:

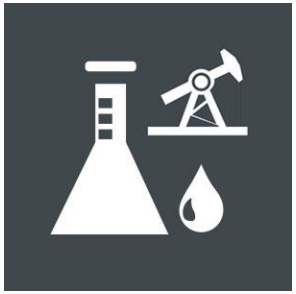
Oxides (Al_2O_3, TiO_2, CeO_2), polymers, various kinds of carbon (activated carbon, nanotubes, graphene)

Types of **nanoparticles** (mono-, bimetallic or ternary alloys) are defined by the project purposes



- High surface area of the support
- Chemical stability
- Resistance to aggressive media
- High dispersity

Applications:



Petrochemistry

Sensors

Medicine

Electromagnetic shielding

Alternative energy

Hydrogen production

Nowadays, much attention is paid to ethanol steam reforming (ESR) due to high-yield hydrogen production. Hydrogen is well known as a promising energy carrier and major candidate to replace hydrocarbon fuels and to solve environmental problems in future.

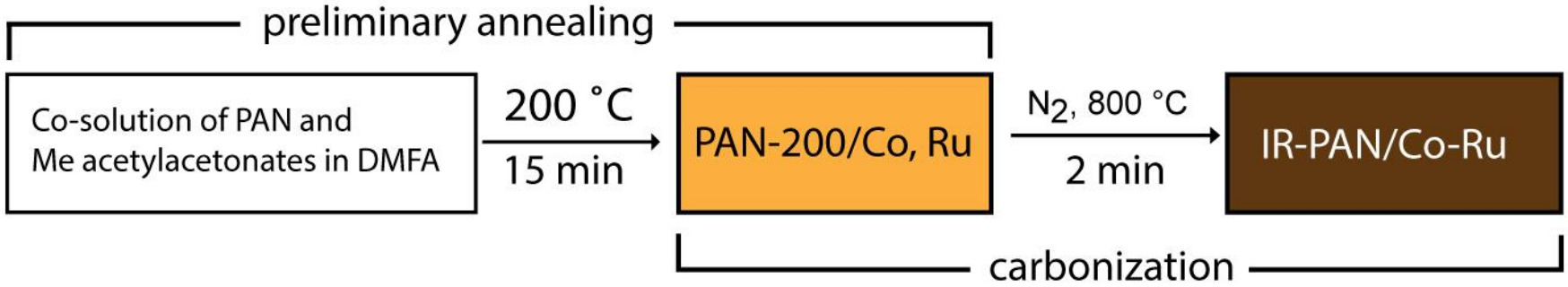
$$C_2H_5OH + 3H_2O \leftrightarrow 2CO_2 + 6H_2$$

The main reaction of ESR gives six hydrogen molecules from one alcohol molecule, but a number of side reactions accompanies it.

Noble metals (Rh, Pt, Pd) are widely known as effective catalysts for existing and prospective industrial processes and ESR as well. However, noble metal based catalysts are expensive. In order to cost-minimize and improve catalytic parameters, the approach of the alloy or bimetallic ‘core-shell’ structured nanoparticles fabrication was proposed.

The metal-carbon nanocomposite preparation

The metal-carbon nanocomposites C/Co-Ru based on polyacrylonitrile (PAN) were prepared under the conditions of IR heating of a precursor obtained according to the following procedure.

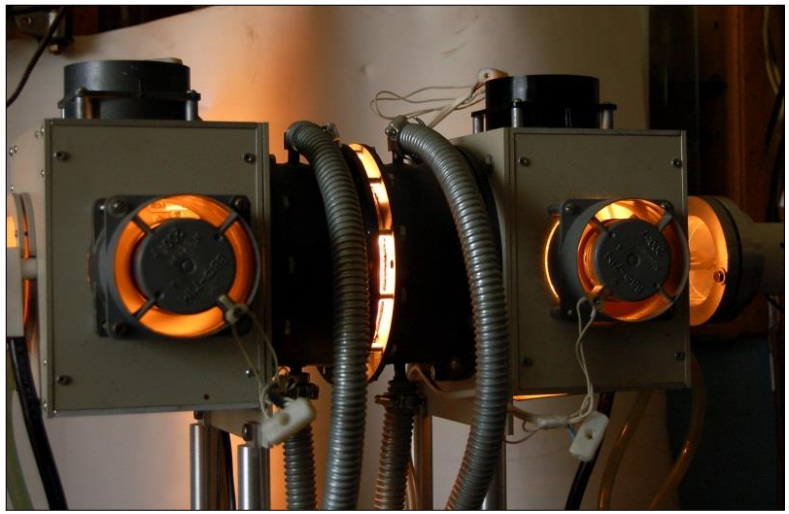


Preliminary annealing:
– solvent disposal,
– tentative structuring

Metal concentration is 1, 5, 10 wt%.
Metal ratio is Co : Ru = 9:1

Carbonization:
– the formation of ordered carbon structures,
– dehydrogenation of the backbone polymer chain of PAN
– efficient reduction of the metal in the presence of hydrogen

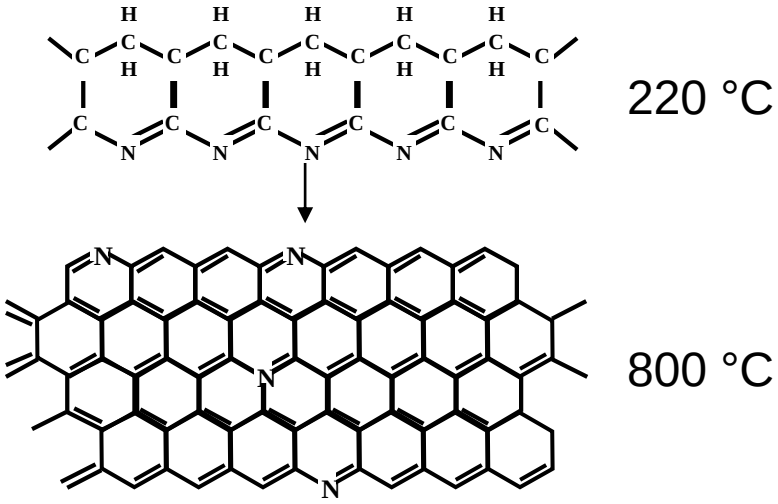
IR radiation provides a decrease of carbonization and metallic nanoparticles formation time. It takes only a few minutes for the process instead of several hours for conventional heat treatment.



As result, simultaneous Co-Ru alloy nanoparticles and carbon support formation occur

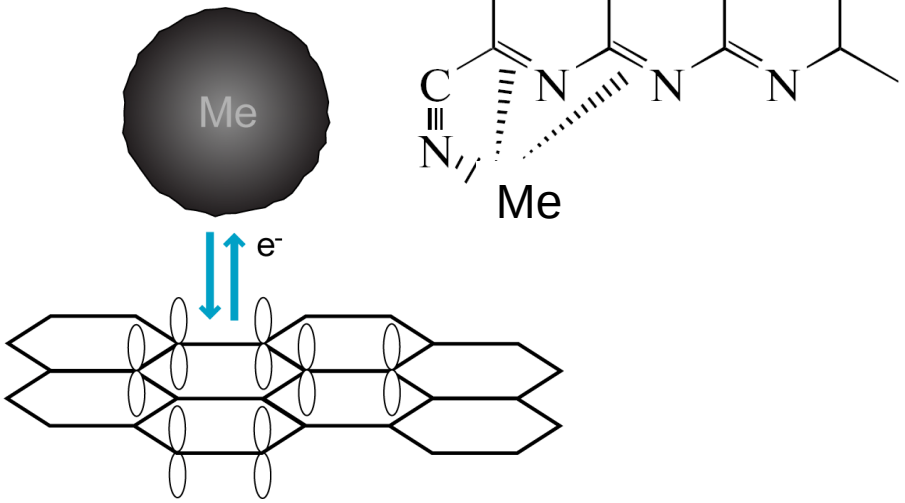
Why polyacrylonitrile?

The chemical transformations of PAN under IR-radiation



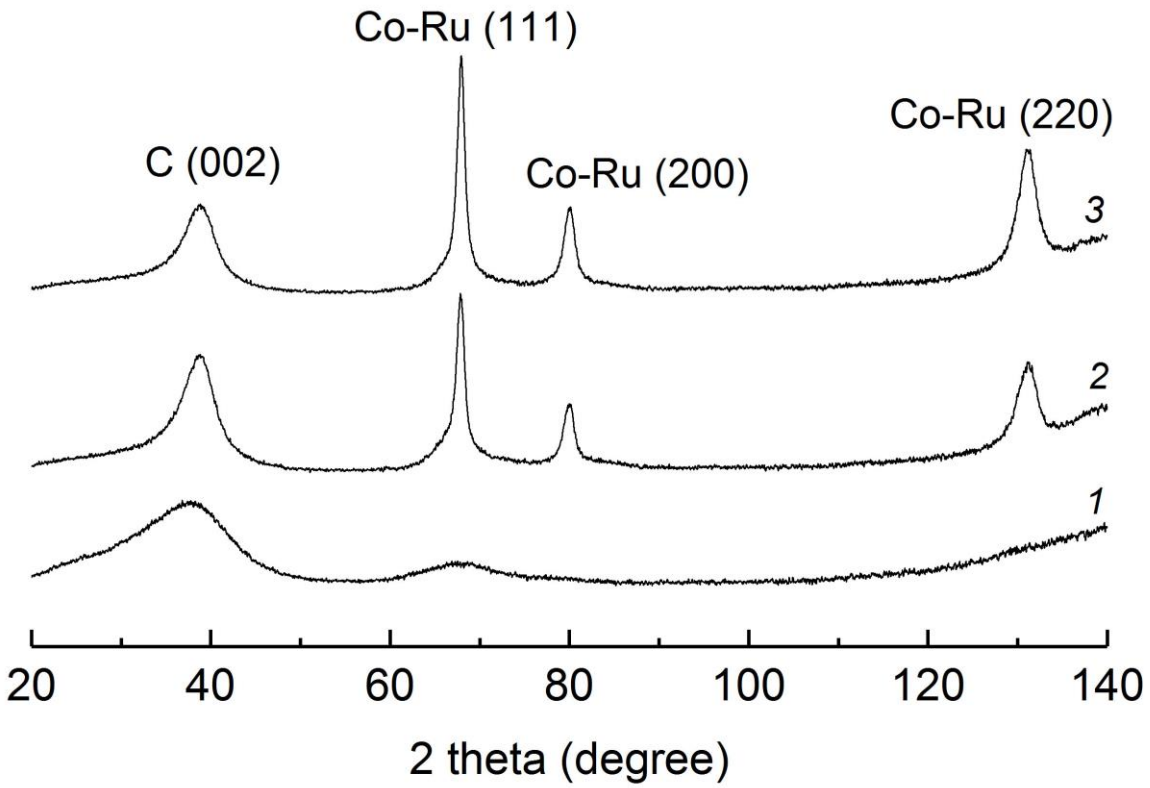
H_2, N_2, NO, NH_3, H_2O, CO, C_3H_6, C_2H_4=NH, CO_2, C_2H_4, C_3H_6, C_3H_8, HCN

The metal ions formed complexes with the conjugation system being formed and bound to –CN terminal groups and the nearest conjugated bonds –C=N–C=N–.



Hydrogen released as a result of dehydrogenation of the backbone polymer chain reduces metals. The IR treatment of the precursor based on the co-solution of the polymer, cobalt and ruthenium compounds leads to a simultaneous bimetallic nanoparticles and carbon support formation.

XRD study

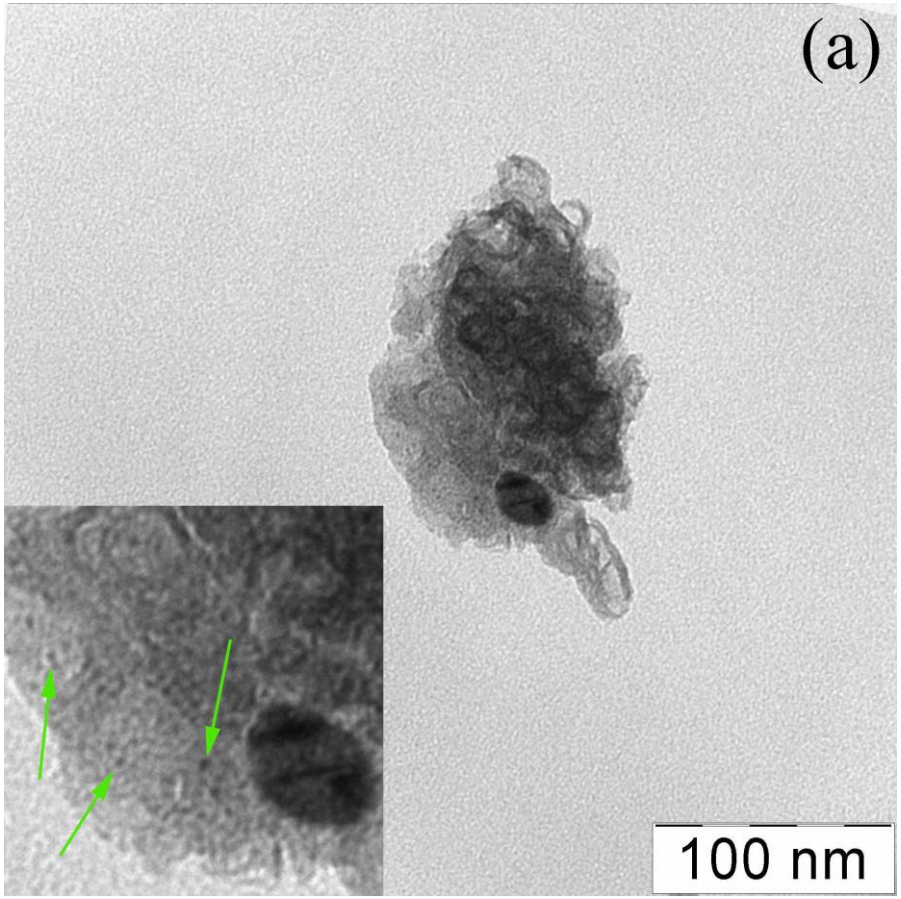


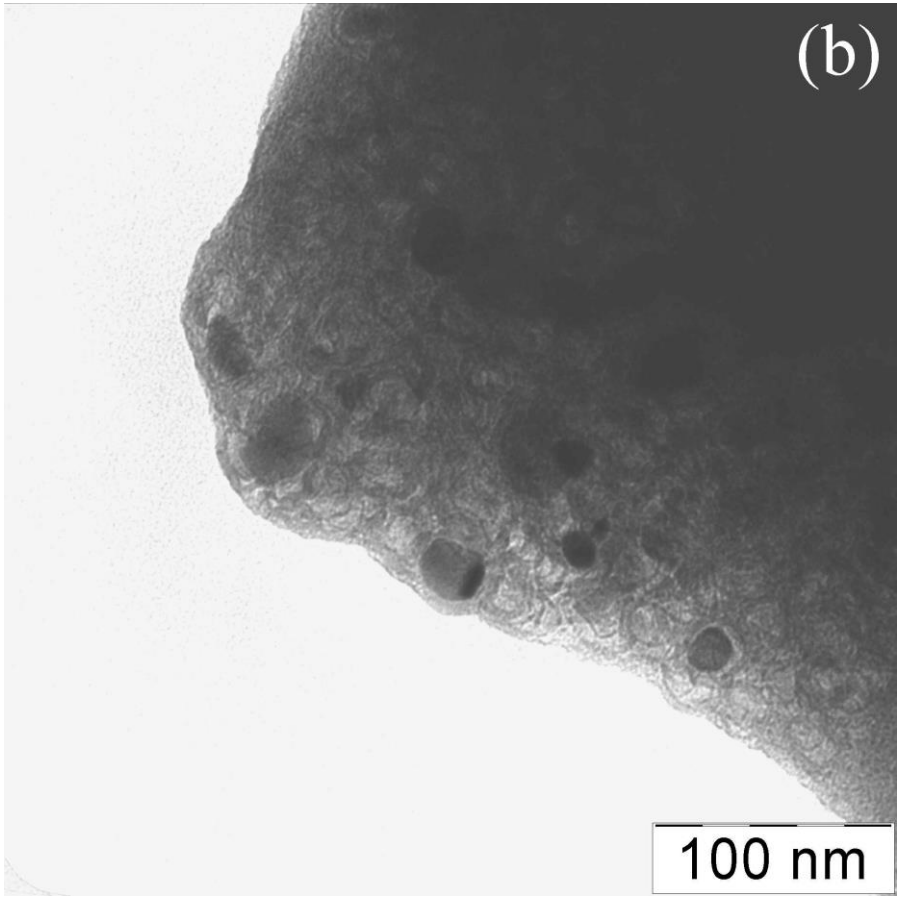
XRD patterns of metal-carbon nanocomposites C/Co-Ru with different metal loading:
1 (*1*), 5 (*2*) and 10 wt% (*3*)

According to Inductively Coupled Plasma (ICP) Spectroscopy, the Me content in the nanocomposites is:

Metal loading, wt%	ICP data, wt%
1	1.08
5	6.09
10	10.51

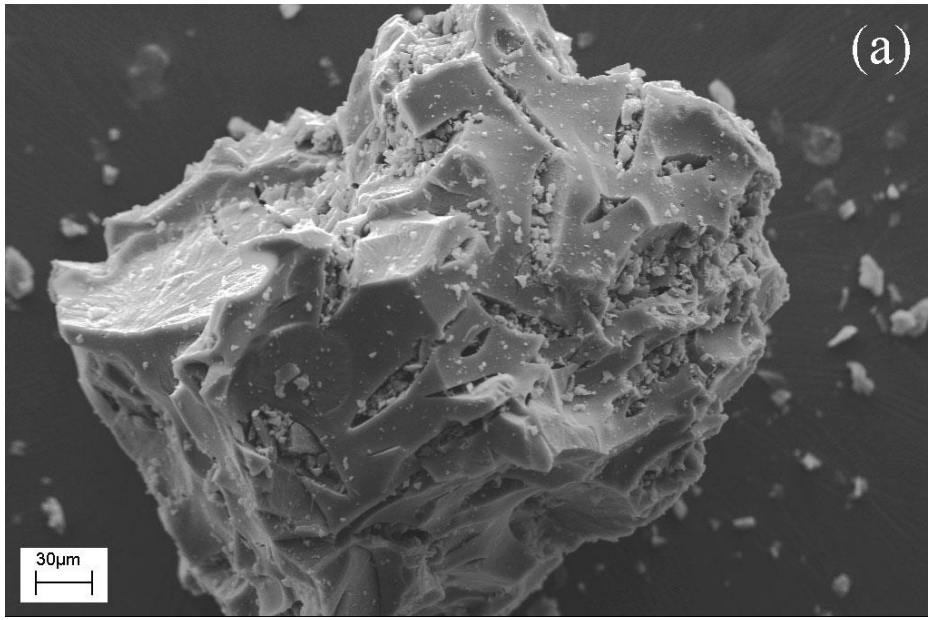
Transmission electron microscopy

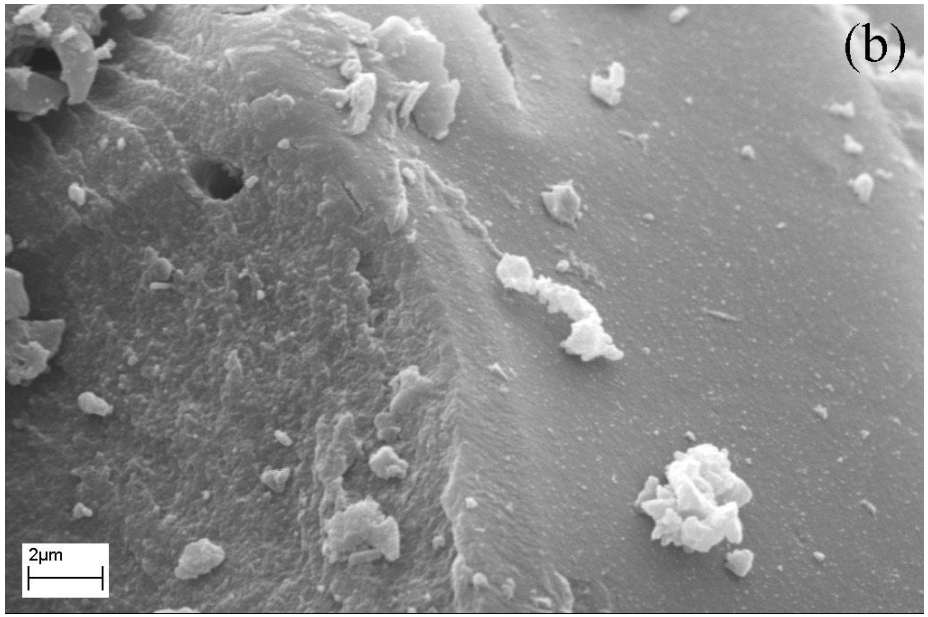




Metal nanoparticles are observed inside some rounded carbon shells. Co-Ru nanoparticles size is about 15-30 nm. However, the image (a) reveals the presence of much smaller metal nanoparticles, which have a diameter of 2-4 nm

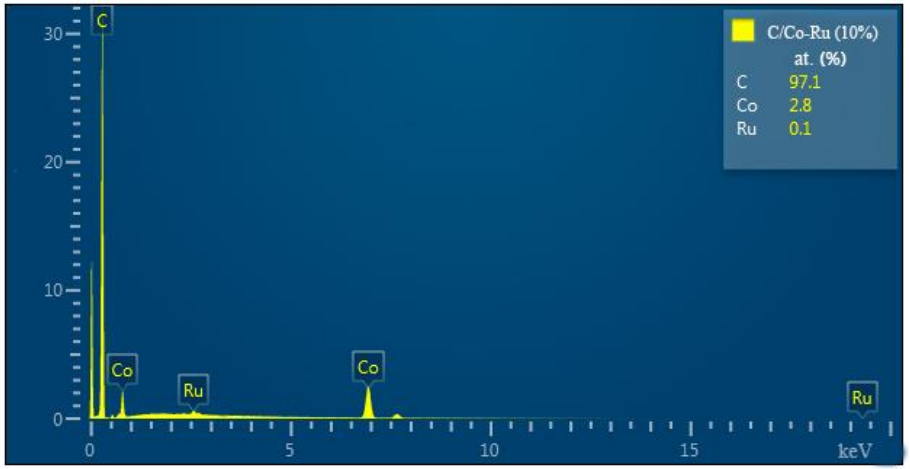
Scanning electron microscopy



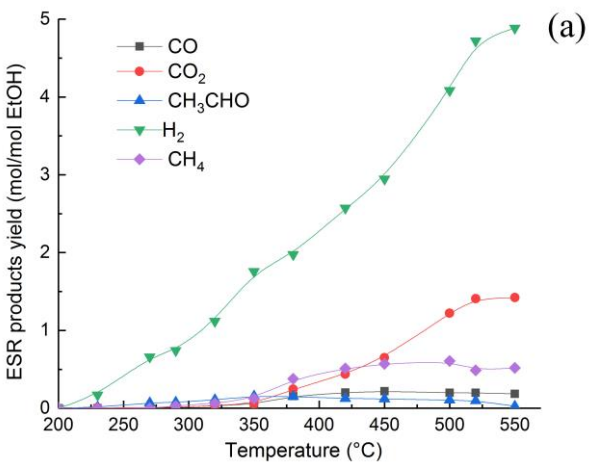


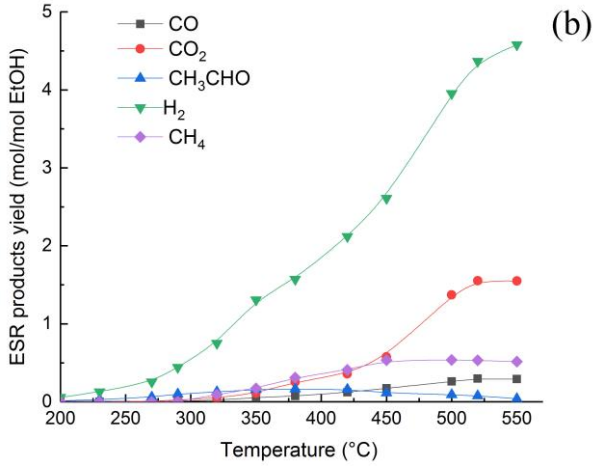
The samples are characterized by a dense bulk morphology with crater- and cavern-rich damaged surface

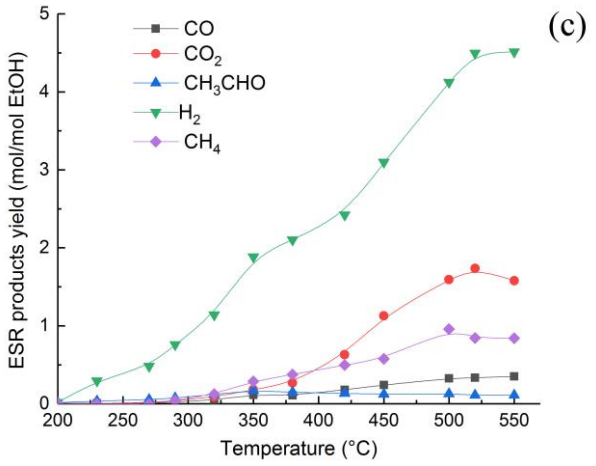
Element	Content, wt %
C	87.13
Co	12.24
Ru	0.63



Ethanol steam reforming







The obtained samples were tested for catalytic activity in ESR reaction at temperatures up to 550 °C. As a result of the reforming a mixture of hydrogen, carbon oxides, methane and acetaldehyde is obtained. The molar ratio H_2O/EtOH was 3.

This study showed that the catalytic activity of all three samples was very similar and did not significantly depend on the metal loading. However, it is noticeable that methane formation increased as metal loading increased.

The prepared catalysts did not require an additional stage of preliminary hydrogen treatment at high temperatures to activate the catalyst. As shown in Table, no crucial change in the hydrogen yield for the catalysts before and after hydrogen activation procedure was observed.

Metal loading, wt%	H_2 yield after hydrogen activation stage, mol H_2/ mol EtOH	H_2 yield without hydrogen activation stage, mol H_2/ mol EtOH
1	4.89	4.6
5	4.58	4.51
10	4.51	4.5

Conclusions

•Bimetallic Co-Ru nanoparticles supported on PAN-derived carbon were successfully prepared via IR pyrolysis of the precursor based on joint solution of PAN and metal compounds.

•The simultaneous PAN-based carbon and Co-Ru solid solution nanoparticles formation was demonstrated.

•The high yield of hydrogen was recorded for all three samples, whereas the by-product yield was relatively low.

•The study of the metal loading effect on hydrogen yield gave the following row of the activity: C/Co-Ru (1%) > C/Co-Ru (5%) > C/Co-Ru (10%).

•Futhermore, it was shown that developed procedure of the metal-carbon nanocomposite preparation provides the production of the catalysts, which do not require an additional stage of preliminary hydrogen treatment at high temperatures to activate the catalyst.