Preparation and catalytic study of novel highly porous metal-carbon nanocomposites based on bimetallic Co-Ru nanoparticles

M N Efimov¹,³, E Yu Mironova¹, A A Vasilev¹,², A A Pavlov², D G Muratov¹,², E L Dzidziguri² and G P Karpacheva¹

¹ Topchiev Institute of Petrochemical Synthesis RAS, Moscow, 119991, Russia
² National University of Science and Technology «MISiS», Moscow, 119049, Russia
³ Corresponding author: efimov@ips.ac.ru

Abstract. Novel method involving simultaneous formation of highly-porous carbon support and bimetallic Co-Ru nanoparticles was proposed. Joint solution of polycyronitrile and metal compounds in dimethylformamide was employed as a precursor of metal-carbon nanocomposites. Applying of infrared heating on the precursor allowed to reduce fabrication time of the nanocomposites significantly. The evolution of Co-Ru solid solution depended on synthesis temperature was studied. The specific surface area of metal-carbon nanocomposites dependence on temperature synthesis was shown as well. It was found that IR annealing of the precursor at 700-800 °C led to carbon matrix formation with specific surface area of about 1300 m²/g. The carbon-supported bimetallic Co-Ru nanoparticles obtained at 800 °C were tested as catalysts in hydrogen production via ethanol steam reforming. The high yield of hydrogen was recorded, whereas by-product yield was relatively low.

1. Introduction
At present, a development of new and an improvement of existing production methods of nanomaterials with tailored properties is one of the major scientific and industrial tasks. Typically, the nanocomposites consist of two components: support and filler [1]. Carbon is one of the most promising support type due to its high specific surface area (SSA), chemical resistance to aggressive media, electrochemical and catalytic properties, low cost [2]. Various types of carbon are well known and studied, namely, single- or multi-walled nanotubes, ultradispersed nanodiamond, graphene, graphite, fullerenes, etc [2-6]. Activated carbon (AC) takes a special place among these different carbon supports due to all above mentioned advantages of carbon and especially extremely high SSA, a numerous carbonaceous precursors and opportunity to tune its structure and properties [6-8]. AC is formed via physical or chemical activation of carbonaceous precursors with water steam or chemical activating agents, i.e. alkali, acids or metal salts. The chemical activation gives more flexible route of highly porous carbon formation and provides larger SSA. Carbon support can be obtained from many types of carbonaceous precursors such as coal, natural and synthetic polymers, etc [9-11]. In general, the functional properties of nanocomposites are provided by metal nanoparticles as a filler which can have catalytic, medical and antibacterial, ferromagnetic and other various features. In order to improve functional properties or expand the scope of possible applications, the preparation of alloy or bimetallic nanoparticles is suggested [12].
For years, growing demand for functional materials which can be employed as heterogeneous catalysts for multiple industrial chemical reactions is observed. Much attention is paid to hydrogen production from renewable sources such as ethanol. Hydrogen is well known as a promising energy carrier and major candidate to replace hydrocarbon fuels and to solve environmental problems in future. Hydrogen production via ethanol steam reforming (ESR) is extensively studied [13-15] due to high-yield hydrogen production. Among the various feedstock alternatives, bio-ethanol is very promising non-toxic and high hydrogen content source.

Noble metals are widely known as effective catalysts for existing and prospective industrial processes such as ESR. However, noble metal based catalysts are expensive. In order to cost-minimize, the approach of the alloy or bimetallic ‘core-shell’ structured nanoparticles fabrication was proposed [15]. To date the most general metal-carbon catalyst preparation method employs a wet synthetic chemistry, which involves the reduction of metal precursors in a solvent and impregnation of a carbon support with it. This strategy needs a preparation of a carbon support at first and at the second stage an introducing metal nanoparticles is carried out followed by heating for several hours or applying chemical metal reduction. Polymers employed as carbon precursors for a support and IR radiation heating provide a tremendous reduction in the time of metal-carbon nanocomposites synthesis [16, 17].

In this paper, one-step procedure of highly porous metal-carbon nanocomposite preparation based on IR pyrolyzed polyacrylonitrile (PAN) and Co-Ru nanoparticles was proposed. We studied the evolution of Co-Ru solid solution and SSA of the nanocomposites depended on synthesis temperature. The obtained nanocomposites were tested as catalysts in ESR.

2. Experimental

2.1. Materials
Polyacrylonitrile ($M_n = 79\times10^3$, $M_n/M_w = 3.54$) was synthesized according the procedure described in [18]. Cobalt acetylacetonate (Acros Organics, 99%), ruthenium acetylacetonate (Sigma-Aldrich, 97%), dimethylformamide (Fisher Chemical, synthesis grade) and KOH (Fisher Chemical, laboratory reagent grade) were used as obtained. Bidistilled water was used for KOH aqua solution preparation.

2.2. Sample preparation
The metal-carbon nanocomposites were prepared under the conditions of IR heating in the laboratory device of incoherent IR annealing [17, 18]. The halogen lamps KG-220 (total power of 24 kW) were applied as radiation source, which had maximum emission wavelength in the region of 0.9–1.2 µm. The samples synthesis temperature range was 500–900 °C. The co-solution of the polymer and metal acetylacetonates in dimethylformamide was dried at 80 °C. The weight ratio of carbon containing in PAN to total metal amount was 5:1 for all material studies and 10:1 for catalytic tests. The Co:Ru weight ratio was 9:1. The obtained film was chopped and pre-carbonized at 200 °C in air for 20 min. The pre-carbonized precursor was milled and impregnated with aqua solution of alkali for 24 h. The weight ratio of the pre-carbonized precursor to KOH was 1:1. Then a sample was dried until constant weight and placed into the IR annealing device. Main heating step was performed at desired temperature for 2 min with a heating rate of 3000 °C/h in the nitrogen atmosphere. The sample for catalytic test was synthesized at 800 °C. The samples were marked as IR-PAN-Co-Ru-x, where x - is a synthesis temperature.

2.3. Sample characterization 
Powder XRD analysis was performed using a diffractometer “Difray” 401 with Bragg–Brentano focusing, using Cr-Kα radiation in the continuous mode (wavelength 0.229 nm) at room temperature. The average coherent scattering regions (CSR) size was calculated by the Selivanov–Smyslov method from the broadening of the diffraction peaks. The morphology of nanopowders was studied with LEO912 AB OMEGA transmission electron microscope. BET surface area test was conducted on Accusorb 2100 at 77 K in the region of relative pressure ($P/P_0$) from 0.01 to 0.99.
The activity of catalysts in ESR was tested in a stainless fixed-bed tubular reactor. The ESR reaction was carried out at 250-550 °C under atmospheric pressure. The liquid solution with a water-to-ethanol molar ratio of 3 was fed through a syringe pump (Instilar 1488 Dixion) at a flow rate of 2 mL/h into a heated chamber to evaporate the solution. The gas products were analyzed by a gas chromatography.

3. Results and discussion
It was proved that IR annealing is more efficient route to carbonize the polymer and to activate carbon as well [17, 18]. 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.

The XRD phase analysis presented in Figure 1 displays reflection peaks corresponded to carbon, α-Co- and β-Co-based Co-Ru solid solution phases at 62, 72 and 68, 80, 132°, respectively. The graphite reflection peak at 39° becomes sharper and β-Co diffraction peak shifts to small angles as the synthesis temperature increases. PAN graphitization process and the cobalt-containing nanoparticles presence may lead to structured carbon formation indicated by this reflection peak. The Co-Ru reflection peak intensity increase is observed as synthesis temperature rises due to an increase of Co-Ru crystallites size. Ruthenium diffraction peaks are not observed since the Co-Ru solid solution has been formed.

![Figure 1: XRD patterns of IR-PAN-Co-Ru samples obtained at 500 (1), 600 (2), 700 (3), 800 (4) and 900 °C (5).](image)

The co-solution of the polymer and metal salts and the presence of alkali leads to simultaneous bimetallic nanoparticles creation, carbon support formation and its activation. Figure 2 demonstrates a distribution of metal nanoparticles in the highly porous PAN-based carbon obtained at 700 and 800 °C. TEM images reveal two types of carbon, namely, soft porous carbon matrix and structured graphite shells covering metal nanoparticles. Such ordered carbon shells provide graphite reflection peak at 39° in XRD pattern.
In order to study an effect of alkali presence on PAN-derived carbon support during nanocomposite synthesis the nitrogen adsorption measurements were performed. The results of BET analysis are shown in Table 1.

![Figure 2. TEM images of IR-PAN-Co-Ru obtained at 700 (a) and 800 °C (b).](image)

According to BET method the specific surface area values of IR-PAN-Co-Ru increased as preparation temperature rises and started decrease above 700 °C. In most studies, temperature of about 800 °C was found to be optimal for activated carbon preparation [19]. In our case, the maximum specific surface area of 1361 m²/g was obtained at 700 °C, whereas the nanocomposite synthesis at 800 °C led to formation of the sample with specific surface area of 1230 m²/g. This fact can be explained by the presence structured carbon shells around Co-Ru nanoparticles. Such metals as cobalt, iron or nickel are known to be very effective in conversion of amorphous carbon in graphite structures [20]. These graphite-like shells formed more intensively at higher temperature reduce the specific surface area since a structured carbon reacts with alkali less readily. Thus, heating at 700 °C provides maximum specific surface area of metal-carbon nanocomposites based on Co-Ru nanoparticles.

In Table 1, the values of lattice parameters for (111), (200) and (220) planes are demonstrated. The lattice parameter of bulk cobalt 0.3544 nm. As shown in Table 1, in all samples, a minor increase in the lattice period is observed for all samples in comparison with the reference data due to formation of solid solution of ruthenium in cobalt.

Table 1. Values of lattice constants of metal phase in IR-PAN-Co-Ru samples obtained in the temperature range 500-900 °C.

| T, °C | a(111), nm | a(200), nm | a(220), nm | S_{BET}, m²/g |
|------|------------|------------|------------|---------------|
| 500  | 0.3549     | 0.3550     | 0.3544     | 538           |
| 600  | 0.3556     | 0.3554     | 0.3547     | 623           |
| 700  | 0.3559     | 0.3556     | 0.3550     | 1361          |
| 800  | 0.3560     | 0.3556     | 0.3549     | 1230          |
| 900  | 0.3565     | 0.3560     | 0.3550     | 828           |
The sample IR-PAN-Co-Ru-800 was chosen for catalytic test in ESR process due to it was proved to be very promising reaction for hydrogen production. The main reaction of ESR gives six hydrogen molecules from one alcohol molecule (1), but a number of side reactions accompanies it:

\[ \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 6\text{H}_2 \quad \Delta H^{\circ}_{298\text{K}} = +173 \text{kJmol}^{-1} \]  

As a result of the reforming a mixture of hydrogen, carbon oxides, methane and acetaldehyde is obtained (Fig. 2). The main products of ESR on the catalysts were H\(_2\) and CO\(_2\), while the yields of CH\(_4\), CO and acetaldehyde were comparatively low. The ethanol conversion reached 99\% at 550 °C. No catalyst's deactivation was detected during experimental tests.

![Figure 3. The ESR products yield per mole of ethanol on IR-PAN-Co-Ru-800.](image)

In summary, effective active metal-carbon catalysts based on bimetallic Co-Ru nanoparticles supported on highly porous IR pyrolyzed polyacrylonitrile were prepared. Since this method is scalable, cost-efficient and provides a tuning of structural characteristics during the material synthesis, it can be proposed as very promising route for industrial fabrication of metal-carbon nanocomposites with desired properties.

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