Perspective of nanochemistry in oil industry

Prof. A. Shabanov, U. Gasanova

Nanotechnology appears to be one of the most important and exiting area of knowledge on the first line of physic, chemistry, biology and medicine. Nanotechnology gives a great hope on quick hitch and new directions of technology development in many spheres of activities, including oil production and oil chemistry.

Notwithstanding of the word nanotechnology is relatively new, nanoscale devices and structures are not new. In fact they have existed since the beginning of a life on the Earth. For example mollusk sea ear creates strongly constructed, being iridescent shell. Mollusk glues together the firm particles of chalk by special mixture of carbohydrates and peptides. The crackers appeared on the shells surface do not spread inside of shell due to firm nano-constructed building blocks. Hence shells are the natural evidence of nano-constructed structures which are much more firm than homogeneous substances.

The exact time of the first usage of advantages of nanoscale materials is unknown. There are intelligences related to IV century B.C. concerning roman glass makers made the glass, containing metals nanoparticles. The good of that period, called Lycurgus bowl is exhibited in Britain museum. The bowl showing the death of King Lycurgus is made of glass, containing the gold and silver nanoparticles. The color of this bowl changes green to dark red by placing the light inside it. The variety of colors of wonderful stained-glass windows is explained by the presence of metals nanoparticles.

In 60^{th} of 20th century had been carried out the experiments on small particles of metals. In that period of time it was not called nanotechnology, and as a matter of fact was not the one. One of the works of that period was related to creation of nanoparticles of alkali metals by evaporation of Na and K and further precipitation of them on coller lining. A unique aspect of nanotechnology is the vastly increased ratio of surface area to volume present in many nanoscale materials which opens new possibilities in surface-based science, such as catalysis. Nanotechnology and nanoscience got started in the early 1980s with two major developments; the birth of cluster science and the invention of the scanning tunneling microscope (STM).

A lot of global environmental problems are still waiting its solution. According to the prognosis nanotechnology will be able to solve these problems. So petrol engeneers are still searching the modern methods for increasing of the layer pressure. And some success has been reached in this term, but there is no drastic geotechnological approach, allowing to extract residuum oil from old explored oilfields. For the first time the application of nanotechnological approach for increasing of the layer pressure was suggested by Azerbaijani scientists. Academician Azad Mirzajan-zadeh first suggested the method for increasing of the layer pressure with application of nanochemical method. The scientists from SRI “Geotechnological problems of oil, gas and chemistry” carried out the application of iron nanocomposite for increasing of the layer pressure of the system in pilot plant. However it should be noted that only 0,5-0,7% nanoparticles of metal, were produced by mechanical breaking up and further extraction by ether. Nanoscale metal particles retained in the ether, giving ultra disperse system due to its high chemical activity. And thanks to this high activity it was possible to separate nanoscale metal particles from the precipitated inactive metal particles.

Further the group of scientists from SRI “Geotechnological problems of oil, gas and chemistry” under the scientific leadership of professor Shabanov Alimamed developed the chemical method of preparation iron nanoparticles, on the basis of reducing Fe(II) salt by sodium tetrahydridoborates. The essence of this process is reaction of Fe(II) salt with sodium tetrahydridoborates at the presence of diazacrown ethers. The reaction of Fe(II) salt with sodium tetrahydridoborates leads to formation iron tetrahydridoborate, and the latter decomposes with producing iron hydride and borane:

$$FeSO_4 + 2NaBH_4 \rightarrow Fe[BH_4]_2 + Na_2SO_4$$

$$Fe[BH_4]_2 \rightarrow FeH_2 + 2BH_3$$

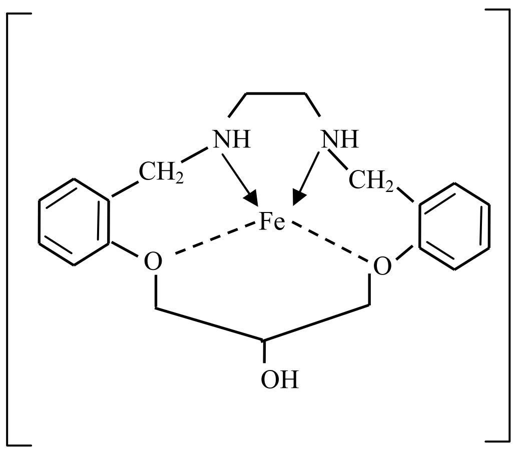
$$6FeH_2 \rightarrow Fe_6 + 6H_2$$

But producing iron hydride does not allow to obtain Fe_6 nanoscale particle with high yield. With the aim to increase the output of Fe nanocomposite have been suggested the application of interphase catalysis method. So the interphase catalysis method was carried out in double-phase system water-butanol 1:1at the presence of diazacrown ether.

$$FeSO_4 + 2NaBH_4 \rightarrow Fe[BH_4]_2 + Na_2SO_4$$

$$Fe[BH_4]_2 + CW \rightarrow FeCW[BH_4]_2$$

$$Fe\,CW[BH_4]_2 \rightarrow CW + Fe + 2BH_3 + H_2$$



$(BH_4)_2$

In accordance with this scheme Fe(II) salt with sodium tetrahydridoborate are placed in the system water-butanol 1:1, and then diazacrown ether is added. After 2 hours obtained iron tetrahydridoborate fully transmits into the organic layer, due to interphase catalysis, which is carried out by CW. The organic layer is come off and heated for separation of butanol. During this process complex decomposes on initial CW, iron tetrahydridoborate, the latter decomposes by heating with producing of highly dispersed nanoscale iron particles Fe_6 and borane. Composition of Fe_6 was established by mass-spectroscopy method.

The application of metal nanoparticles in the process of methane burning at low temperatures attracts a great interest of scientists. The burning of methane at the temperatures above 1200^0C leads to producing the harmful nitrogen oxides NO_x, which are the ingredients of photochemical smog. From this point of view it is extremely important to search the new catalysts for oxidation of methane. We developed the synthesis of new catalyst for oxidation of methane at the temperatures less than 400^0C. With this aim we carried out the reducing of the mixture of $Ba(OCH(CH_3)_2)_2$ and $Al(OCH(CH_3)_2)_3$ in mole ratio 1:6 in isopropyl alcohol by metallic sodium at the present of diazahydroxy substituted dibenzo-15-crown-4.

$$Ba(OCH(CH_3)_2)_2 + Al(OCH(CH_3)_2)_3 \rightarrow BaAl_6$$

Obtained nanoscale $BaAl_6$ is catalyst in the process of methane burning at low temperatures.

Materials reduced to the nanoscale can suddenly show very different properties compared to what they exhibit on a macroscale, enabling unique applications. Some of these materials, that are inert at normal scales, can serve as a potent chemical catalyst at nanoscales. Much of the fascination with nanotechnology stems from these unique quantum and surface phenomena that matter exhibits at the nanoscale. And such phenomena was discovered when we carried the metallization reaction of alkyl aromatic hydrocarbons at the presence of crown ethers and cryptands. The substitution of hydrogen atom in hydrocarbons and other organic compounds is a matter of great scientific and practical interest. This process is especially important in terms of carrying out the subtle organic synthesis. But the direct substitution of hydrogen atom in hydrocarbons in alfa position relatively benzene ring by sodium or potassium is practically impossible. In order to increase the basic properties of nanoparticles of sodium or potassium, which are able to substitute the hydrogen atom in alkyl aromatic hydrocarbons, we suggested the method to obtain the nanoparticles of some alkali metal. Using the high velocity mixer (10000 revolutions per minute) we got the high dispersed emulsion of sodium or potassium in alkyl aromatic hydrocarbons (benzene, toluene, isopropyl benzene). Further we add the macrocyclyc compound in the high dispersed system of alkali metal/alkyl aromatic hydrocarbons. In carrying out this process the solvation of alkali metal with changing of the color grey to bluish-violet was observed. The essence of solvation of alkali metal is in formation of complex crown ether/alkali metal (I) and (II), due to including the cation of alkali metal in crown ether cavity. As the result of this process in the anion part of such complex nanoanions K_7^- and Na_7^- are formed

$$K^0 + L \rightarrow [LK^+]K_7^- \qquad Na^0 + L \rightarrow [LNa^+]Na_7^-$$

I **II**

Nanoanions K_7^- and Na_7^- display the high chemical activity and are able to substitute the hydrogen atom in alfa position relatively benzene ring in alkyl aromatic hydrocarbons. Hence the reaction of complex I with toluene leads to producing the potassium-organic derivative V, and then this potassium-organic derivative V reacting with carbon dioxide produces the potassium salt of phenyl acetate VIII or the potassium salt of dimethyl phenyl acetate.

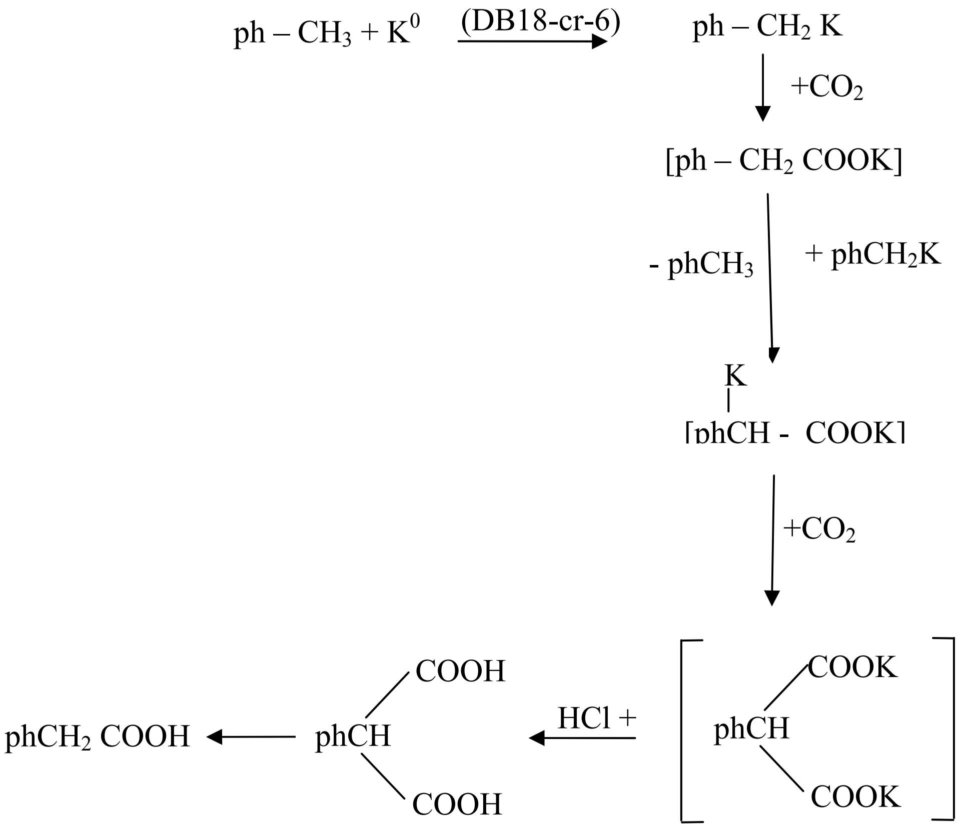
$$Ph{-}CH_3 + [LK^+]K_7^- \rightarrow [LK^+]K_7^- \cdots H{-}CH_2{-}Ph \quad \textbf{(III)}$$

$$\downarrow$$

$$[LK^+]—OCO—CH_2—Ph\ \mathbf{(VI)} \leftarrow\ CO_2 + [LK^+]—CH_2—Ph\ \mathbf{(V)} + HK_7\ \mathbf{(IV)}$$

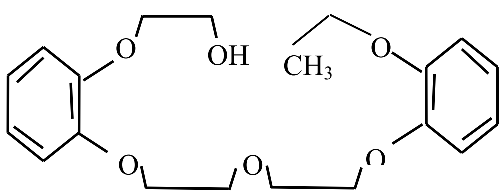
$$\downarrow + HK_7$$

$$[LK^+]K_7^- + HOOC—CH_2—Ph$$



VIII VII

The chemical activity of nanoanions K_7^- and Na_7^- is so high that they are able consequently to substitute the first hydrogen atom, and then the second hydrogen atom in alfa position in alkyl aromatic hydrocarbons, giving correspondingly the potassium salt of phenyl acetate VIII or the potassium salt of phenyl malon acid VII. It should be also noted that the carrying out of the reaction at the temperature above 90^0C leads to opening of crown ether ring with formation of IX.



IX

And as we see now by means of nanotechnology modern synthetic chemistry can reach the point where it is possible to prepare the molecules to almost any structure. These methods are used today to produce a wide variety of useful chemicals such as pharmaceuticals, commercial polymers or catalists for oil production and oil chemistry.