THE EFFECT OF THE STRUCTURE OF NANOCARBON CARRIER ON CATALYTIC PROPERTIES OF PLATINUM-RUTHENIUM ALLOY

Ermilova M.M., Efimov M.N., Zemtsov L.M., Karpacheva G.P., Kulakova I.I., Orekhova N.V., Tereshchenko G.F.

Topchiev Institute of Petrochemical Synthesis RAS, 29, Leninsky av., 11991 Moscow, Russia

Fax: 7 (495)633 85 20 E-mail: ermilova@ips.ac.ru

Introduction

Carbon materials, prepared by polymer carbonisation, arouse a great interest as catalysts supports, providing a high specific area of active metals and stable dispersion of their particles. The method of IR-pyrolysis of precursors based on polyacrylonitrile (PAN) and metal salts, developed in TIPS RAS, allows the incorporation of the active metal nanoparticles into carbon matrix already at the stage of carbonization, due to metal reduction by hydrogen, formed during dehydrogenation of main polymer chain [1]. The additional modification of catalytic properties may give the introduction in IR-pyrolysis precursor of carbons of different nature.

This work studies the influence of the addition of different carbon components (fine dispersed active carbon, carbon nanotubes, detonation nanodiamonds) to IR-pyrolysis precursor on catalytic activity platinum-ruthenium-carbon nanocomposites (IR-PAN/Pt-Ru) in modeling reaction of cyclohexane dehydrogenation.

Results and Discussion

Platinum-ruthenium-carbon catalysts of cyclohexane dehydrogenation were prepared by IR-pyrolysis of precursors based on PAN and $PtCl_4$ and $RuCl_3$ salts by the method described in [2]. Extra carbon component such as multiwalled carbon nanotubes (MCNT), purified finely dispersed coal SKT-6A and ultradispersed nanodiamonds with different specific area (UDA-1, UDA-2, UDA-3) were ultrasonic dispersed before IR-pyrolysis in DMF solution in a mixture with PAN and metal salts.

It was shown on the example of IR-PAN-SKT-6A/Pt-Ru system that increasing of the platinum metals content in the catalyst from 0.7 mass.% to 2.8 mass.% cause substantial increase of cyclohexane conversion at the same other conditions. So, the following study of the influence of precursor composition on the efficiency of nanocomposite metal-carbon was carried out with catalyst, containing 2.8 mass. % of platinum metals at Pt : Ru ratio equal to 9:1. In accordance with XRD data such ratio of Pt and Ru metals ensures the forming of solid solution in bimetal nanoparticles, if IR-pyrolysis intensity corresponds to the temperatures as high as 700°C [2].

The variation of nature of extra carbon component in IR-pyrolysis precursor showed (Table 1) that substitution of pure IR-PAN carbon matrix of catalyst on that of mixture of IR-PAN and SKT-6A causes the substantial increase of cyclohexane conversion. The more high conversion of cyclohexane was obtained on the catalyst containing ultradispersed diamonds UDA-3.

Table 1. The influence of IR-pyrolysis composition on cyclohexane conversion (X) at 375*°C*

Carbon matrix	$S_{уд.}$, m^2/g	X, %
IR-PAN	**10**	**0,1**
IR-PAN-CNT	**30**	**4,5**
IR-PAN-UDA-1	**120**	**5,2**
IR-PAN-UDA-2	**220**	**20,1**
IR-PAN-UDA-3	**400**	**82,5**
IR-PAN-SKT-6a	**600**	**72,5**

These results are evidently accounted for the increasing in specific area of the catalyst carbon carriers ($S_{sp.}$) at the introduction of finely dispersed coal SKT-6A and ultradispersed nanodiamond UDA-3. As a fact, cyclohexane conversion on metal-carbon-carbon nanocomposite catalysts of different composition increases monotonously with the specific area up to that of 400 m^2/g.

At the same time, the cyclohexane conversion on the PAN-SKT-6A/Pt-Ru was lower than that of on nanocomposite IR-PAN-UDA-3/Pt-Ru, in spite of noticeably lower specific area of the later catalyst. Thus, the value of specific area of carrier is vital but not singular factor, controlling the catalytic activity of metal-carbon composites. Apparently, the catalytically active sites of these catalysts forming also at the influence of the presence and surface concentration of different functional groups, controlling adsorption properties of carbon-carbon composite.

The effect of the PAN:UDA ratio in precursor on the catalytic activity of obtained nanocomposites was shown by example of catalytic system IR-PAN-UDA-3/Pt-Ru (Fig.1).

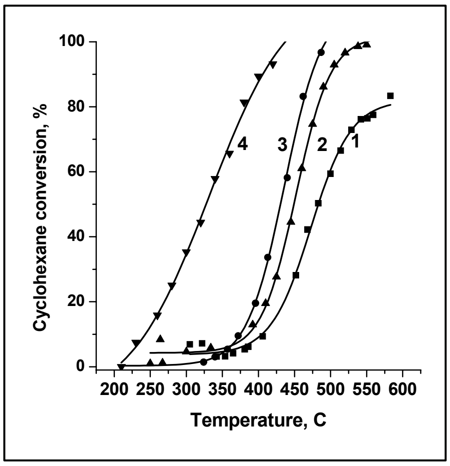


Fig.1. The temperature dependences of cyclohexane conversion on the nanocomposites IR-PAN-UDA-3/Pt-Ru(2.8%) at the PAN concentrations at precursor 0% (1); 1% (2); 5% (3); 10% (4).

As Fig.1 shows, the minimum catalytic activity was obtained at the absence of PAN, that points out on importance of PAN presence in precursor for generation of active sites of metal catalyst and/or for reduction of metal on the stage of composite preparation. The increasing of PAN concentration in precursor up to 10% causes the monotonous rising of cyclohexane conversion.

In the systems IR-PAN-UDA-1/Pt-Ru and IR-PAN-UDA-2/Pt-Ru increase in PAN concentration from 50% to 100% decrease substancially the catalytic activity of metal-carbon-carbon composites (Fig.2) in cyclohexane dehydrogenation.

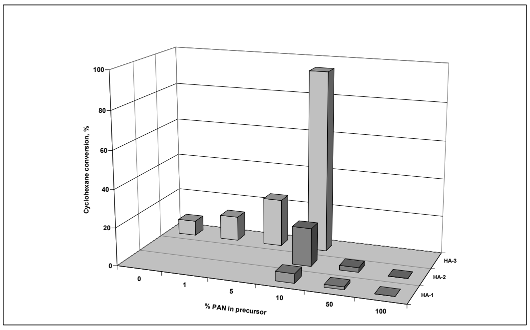
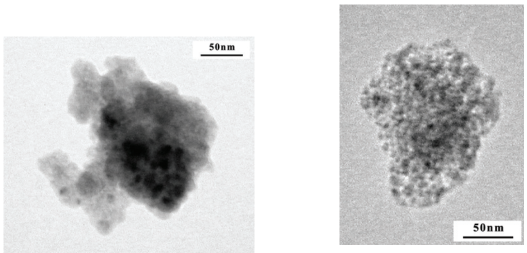


Fig 2. Cyclohexane conversion at 400°C at different nanocomposites PAN-UDA/Pt-Ru(2,8%).

This is accounted for the low specific area of systems with high concentration of PAN. It is confirmed by the data of TEM for the samples PAN-UDA-2/Pt-Ru, containing 50 and 90% UDA-2. Fig.3 shows the different distribution and size of metal particles in these two nanocomposites.



a b

Fig.3. TEM microgrphs of nanocompositeses PAN-UDA-2/Pt-Ru, containing 50% (a) and 90% (b) UDA-2.

Conclusions

It is shown that the addition of extra carbon components (multiwalled carbon nanotubes (MCNT), purified finely dispersed coal SKT-6A and ultradispersed nanodiamonds) to precursor of IR pyrolysis of PAN allows to control the catalytic activity of platinum-ruthenium-carbon nanocomposites (IR-PAN/Pt-Ru) by the increase of specific area of nanocomposite or the concentration of additional carbon component in precursor. The best results in cyclohexane dehydrogenation were obtained at the nanocomposite PAN-UDA-3/Pt-Ru with specific area of carbon carrier 400 cm^2/g and IRPAN:UDA-3 ratio 1:9.

The work was supported by Russian Foundation of Basic Researches (Project № 07-03-00309).

References

1.Zemtsov L.M., Karpacheva G.P, Efimov M.N., Muratov D.G., Bagdasarova K.A. *Russian Polymer Sci. A* 2006.V.48. №6. P.977.

2.Efimov M.N., Zemtsov L.M., Ermilova M.M., Orekhova N.V., Tereshchenko G.F., Dzidziguri E.L., Sidorova E.N. *Bulletin of Lomonosov MIFChT*. 2008. V.3. №1. P. 66.