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ФОРМИРОВАНИЕ Ru НАНОКОМПОЗИТОВ

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В данной работе проведены исследования полимерных иммобилизованных наночастиц Ru путем фронтальной полимеризации (FP) акрилонитрила рутения (AN) в присутствии неорганического носителя и оценка их каталитических свойств в реакции ненасыщенных соединений. На основе акрилонитрильного комплекса рутения синтезирован эффективный и селективный органо-неорганический катализатор и исследована его реакционная способность-активность в реакции гидрирования циклогексена. Синтез акрилонитрильного комплекса рутения на поверхности минерального носителя кремнезема SiO_2, его дальнейшая полимеризация и восстановление приводят к формированию полимер-неорганического композита, включающего наноразмерные частицы Ru, стабилизированные полимерной матрицей, и неорганический носитель. Предложенный метод является новым подходом в подготовке катализаторов. Синтезированные образцы Ru- нанокомпозитов изучены методами элементного анализа, ИК-спектроскопии и рентгенофазового анализа. На рентгенограммах полученных образцов присутствуют широкие дифракционные пики в области от 300 до 800 °С, которые соответствуют кристаллическому рутению. Уширения дифракционных максимумов свидетельствуют об ультрадисперсном состоянии частиц. Для полученных нанокомпозитов характерна микропористая структура с размером пор от нескольких до 20 нм и их равномерное распределение по размеру. Установлено, что удельная поверхность носителей уменьшается после полимеризации RuAN на их поверхности, хотя она больше, чем $S_{уд}$ продукта полимеризации в отсутствии SiO_2. Полученные гибридные нанокомпозиты имеют развитую поверхность и пористую структуру, что обеспечивает доступность активных центров катализатора для реагентов и их высокую активность в исследуемой каталической реакции. На каталитические свойства исследуемых композитов влияют условия формирования Ru-наночастиц, например использование различных режимов фронтальной полимеризации в инертной среде. С повышением температуры восстановительной обработки нанокомпозитов скорость гидрирования на них циклогексена понижается, причиной чего является укрупнение частиц Ru при получении нанокомпозитов при высоких температурах. Следует отметить, что после гидрирования основная масса рутения в поли-RuAN (90%) будет обладать нулевой валентностью. Полимерная матрица также подвергается изменениям, и расширение полос поглощения в спектре N1s подтверждает это. Таким образом, синтезированная гибридизация полимер-иммобилизованных Ru-наночастиц проявляют высокую активность в течение повторных циклов реакции гидрирования циклогексена. Каталитические свойства нанокомпозитов зависят от условий их получения, которые влияют, очевидно, на размер формирующихся наночастиц рутения.

Ключевые слова: нанокомпозиты, комплекс рутения, акрилонитрил, иммобилизация полимерами, каталитические свойства

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FORMATION OF Ru NANO-COMPOSITES

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Researches of polymer immobilized nanoparticles of ruthenium have been carried out by frontal polymerization (FP) of ruthenium acrylonitrile (AN) complex in the presence of inorganic carrier. Assessment of their catalytic properties in the hydrogenation reaction of unsaturated compounds has been done. Effective and selective organo-inorganic catalyst has been synthesized on the basis of akrylonitril complex and its reactivity in the hydrogenation reaction of cyclohexen has been investigated. Synthesis of akrylonitril complex of ruthenium on the surface of mineral carrier SiO_2 silica, its further polymerization and reduction leads to the formation of polymer-inorganic composite including nano-size particle of Ru stabilized by polymer matrix and inorganic carrier. The offered method is a new approach in the catalyst preparing. Synthesized samples of Ru- nano composetes have been studied by methods of element analysis, IR-spectroscopy and X-ray analysis. There are wide diffraction peaks at 300-800 °C range in the X-rays patterns of the obtained samples wich correspond to crystallic ruthenium. Broadening diffraction maximums testifies ultradisperse state of particles. Microporous structure with pore sizes to 20 nm and their uniform size distribution are typical for obtained nano composites. It has been determined that specific surface of carriers decreases after polymerization of RuAN on the surface, though it is bigger than S spec. of the polymerization product in SiO_2 absence. Obtained hybride nano composites have developed surface and porous structure which provide accessibility of active centers of catalyst for reagents and their high activity in the researched catalytic reaction. Formation conditions of Ru nanoparticles influence on catalytic properties of the studied composites, for example, the use of various regimes of frontal polymerization in inert medium. With the increase of the reduction treatment temperature of nano-composites the hydrogenation rate of cyclohexene reduces, the reason of which is the integration of Ru particles in the obtaining of nano composites at high temperatures. It should be mentioned that after hydrogenation the main ruthenium mass in poly-RuAN (90%) will have zero valency. The polymer matrix reduces. It is also subjected to changes and it confirms by spectrum broadening. Thus, the synthesized hybridization of polymer-immobilized Ru-nanoparticles display high activity in the reaction of cyclohexene hydrogenation and keep their activity during repeated cycles of reactions. Catalytic properties of nano-composites depend on the conditions of their obtaining which influence apparently on the size of forming Ruthenium nanoparticles.

Key words: nano composites, ruthenium complex, acrylonitrile, polymer-immobilized, catalytic properties

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INTRODUCTION

Modern synthetic chemistry is focused on obtaining of new materials with a complex of properties and characteristics and also on the development of high-effective methods of their synthesis.

At present researches on obtaining of hybride organo-inorganic matereals with nano-size structures are of great interest.

Materials including a metal nanometer size metal particles have unique physico-chemical properties, and recenly years they have been the object of intense research [1-2]. Their use as a catalyst is particularly interesting. As the atoms on the surface have a higher proportion than the total atoms in the nanoparticles and their catalytic properties can be adjusted by the change of nanoparticles size. Zero-valent complexes and Pd nanoparticles are known as effective catalysts of many organic reactions. Study of ruthenium-another analogue of palladium was of great interest [3-4]. The aim of the work is obtaining of Ru nanoparticles, their fixing on SiO_2 carrier and stabilization by polymer ligand introduction. The goal has been achieved by obtaining polymer-immobilized Ru nanoparticles in the presence of inorganic carrier SiO_2 by polymerization of acrylonitrile complex of Ru nitrate estimation of their catalytic properties in hydrogenation reaction of cyclohexene.

EXPERIMENTAL PART

For synthesis of RuAN modified methodics of akrylonitril complexes of transite metals nitrates has been used. Nitrate and akrylonitrit have been mixed in 1:4 mole ratio in inert atmosphere and grindid to paste state. Then it has been washed by dry ether and dried in vacuum to the constant weight.

Calculated: for RuAN % with
19.4 N 15.0 H 2.7 Ru 28.6
Found % from 20.1, N15.1 H 3.5 Ru 29.4

Obtaining of RuAN on mineral carrier

Synthesis of RuAN in the presence of SiO_2 and C has been carried out on abovementioned methodics from the calculation of Ru content in the catalyst of mixed type- 5-10% mass polymer carrier. Mixture of calculation quantity of Ru nitrate, akrylonitril and SiO_2 (or c) has been grinded in the mill in the box with inert atmosphere to pasteform state, it has been washed with benzone, ether and dried in vacuum not least of 12 h at 30 °C: Content of Ru mass is 5.2% (RuAN/SiO_2).

Frontal polymerization of RuAN and RuAN/SiO_2

For carrying out frontal polymerization, samples RuAN and RuAN/SiO_2 have been preliminarily pressed in the form of tablets with 0.5-0.8 sm diametr, with 1.2-1.5 sm height and 1.45 g/sm^3 density and were placed into glass ampoule. For initiating the polymerization, lover part of ampoule with the sample was immersed into the bath on 0.2 sm depth with heat carrier (Vud alloy) at 80-100 °C temperature. The Reaction rate was estimated due to the displeacement of coloured area front. Powder form polymer and hybride nano-composite products have been washed by methanol and ether and dried in vacuum at room temperature till the constant weight.

HYDROGENATION OF CYCLOHEXENE

The experiments have been carried out in non-continuous glass reactor in the of isopropyle alcohol medium with cyclohexene concentration from $4.7 \cdot 10^{-3}$ to $14.5 \cdot 10^{-3}$ mole/l, constant atmosphere pressure of hydrogen and 20 °C temperature in the condition of intensive stirring. Catalyst sample was given into the reactor from calibrated receiver with water seal. Before the introduction of cyclohexene, the catalyst was subjected to 20 min hydrogen treatment. Reaction rate was calculated graphically on the inclination of initial areas of kinetic curves of hydrogen consumption.

Analysis of catalysis has been carried out by the method of element analysis.

Element composition of the samples has determined atomic-absorption flameless method. X-ray diffraction of powders has been studied on DPOH-2 diffractometer using Cu Kα-radiation. IR spectra of absorption was recorded on-“S pecorol” spectrophotometer.

For obtaining RFE-spectra ES-spectometer-2401 with magnesium anode has been used.

Electron-microscopic researches have been done on transparent electron microscope (TEM) YEOL.

Specific surface of inorganic carrier and polymer-hybride nano-composites and also sizes of pores have been determined on nitrogen adsorbtion at 77 K temperature by static volumetric method on «AUTOSORB-1» device.

RESULTS AND DISCUSSION

AN complex of ruthenium nitrate – Ru(CH_2=CHCN $(NO_3)_2$ - (RuAN) was synthesized by the replacement of crystal water in crystalline hydrate metal nitrate by akrylonitril molecules [5-6]. The results of element analysis and some spectral characteristics of the obtained complex are shown in Table 1.

On the basis of the IR spectroscopic results the metal atom coordination occurs through the oxygen atom of AN ligand carbonyl group (figure 4): in the IR spectrum the bands of carbonyl group passed into long wave area (1667 sm^{-1}), which is typical for similar complexes of transition metals [6].

Table 1

The element composition of ruthenium AN complexes and relative composition of elements on the basis of XPS results

Таблица 1. **Элементный состав комплексов нитрата рутения AN и относительный состав различных элементов на основе результатов РФЭС**

Complex	Element composition, mass. % (found/calculated)				Relative composition, %			
	C	H	N	Ru	C	O	N	Ru
Ru$(NO_3)_2$	-	1.4/1.5	10.3/10.5	40.2/39.9	-	66	22	10.6
RuAN	20.1/19.4	3.5/2.7	15.4/15.0	29.2/28.6	54	26	18	2
RuAN/SiO_2	-	-	-	5.4	15	58	6	0.8

Displacement of spectra C1s (E_{SV} = 288.3 eV), N1s (E_{SV} = 399.8 eV) and O1s (E_{SV} = 531.6 eV) in the XPS (X-ray photoelectron spectra) spectrum, respectively, to high-energy area at 0.5, 0.7 and 0.5 eV also confirms this fact. In the IR spectra of complexes, bands of stretching vibrations of the nitrate anions of 1385 sm^{-1} (NO_3) were also recorded.

In the XPS spectrum presence of $Ru3d_{3/2}$ the presence of low-intensity band with (E_{SV} = 337.2 eV), as well as an increase of the intensity of the band with E_{SV} = 285.7 eV is explained by the creation of π-coordination of the metal atom with respect to double ligand bond. Such phenomenon is not rare for Ru-alkene complexes. The atomic ratio of Ru/N and O/N atoms on the upper layer is equal to 0.11 and 1.4, respectively (Table 1), and the intensity of the band at E_{SV} = 407.2 eV at N1s spectrum (nuclear heat spectrum) ranges 10% of the total weight of the integrated intensity of the whole spectrum. This observation quantitative correlates with the intensity of the line with E_{SV} = 338.8 eV in the $Ru3d_{5/2}$ spectrum (big. 1) and testifies screening of Ru atoms by AAm groups.

It is known that AN complexes of metal nitrates have effective frontal polymerization ability in condensing mode, in frontal regime condition where the conversion of monomer to polymer occurs in the local reaction zone and spreads layer by layer along the whole volume.

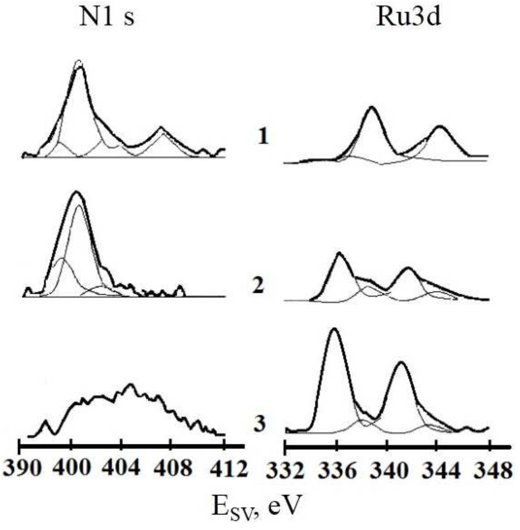

Fig. 1. The XPS spectra of ruthenium nitrate AN complex monomer (1), RuAN after polymerization (2) and RuAN after cyclohexene hydrogenation (3)

Рис. 1. РФЭ спектры мономера акрилонитрильного рутениевого комплекса AN (1), RuAN после полимеризации (2) и RuAN после гидрирования циклогексена (3)

The reaction proceeds in softer mode characteristic for the processes – atmospheric pressure and thermal activation (without the use of chemical activators). In stationary mode, process of polymerization takes place at small temperature range. Heat released from the reaction zone is transferred to the heating zone where the material is heated at the expense of heat exchange, the temperature is increased to such value where the reaction starts, i. polymerization spreading occurs. Start of a short-term reaction is achieved by heating (ignition) one end of the ampoule (15 s). Pressed RuAN monomeric sample this part of the ampoule and its mixture with a mineral carrier has been placed. In this case appearance of the melting zone (transition phase), and change in color from light brown to dark brown black are observed. The rate of reaction can be controlled by color change border displacement. Ignition temperature (80-100 °C) of frontal polymerization of ruthenium AN complexes is significantly lower than the corresponding indices of (170-180 °C) nitrates AN complexes of Co (II), Ni (II), etc.

At the highest ignition temperature (150-170 °C) the eruption of the reaction mass from the glass tube and the transition to the combustion regime is observed, which is obviously due to the formation of Ru pyrophoric fine particles. According to XPS indicators, the main line in the spectrum Ru3d of polymerization products corresponds to E_{SV} = 336.5 eV, which is much larger than E_{SV} on Ru^0 (< 336.0 eV). This can be explained by the formation of Ru^0 and Ru^{b+} fine particles.

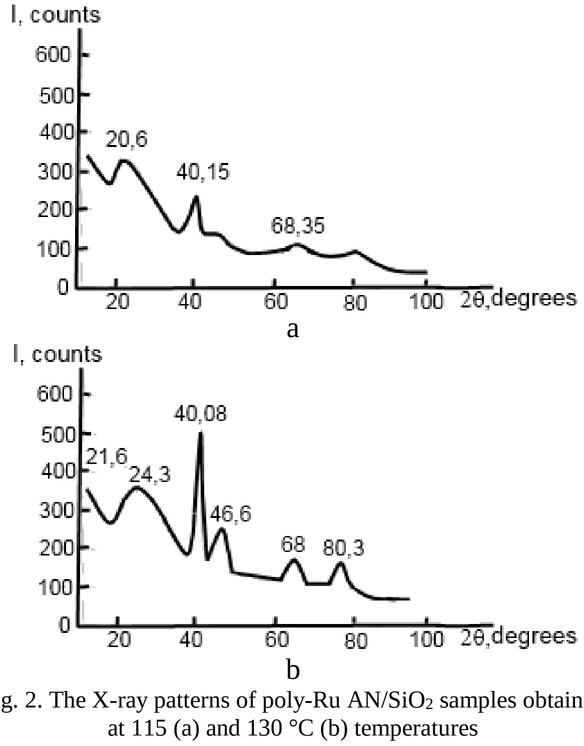

Fig. 2. The X-ray patterns of poly-Ru AN/SiO_2 samples obtained at 115 (a) and 130 °C (b) temperatures

Рис. 2. Дифрактограммы образцов поли-Ru AN/SiO_2, полученных при температурах 115 (a) и 130 °C (b)

In obtaining of nano composite materials use of FP method is of particular interest in developing of polymer-immobilized catalyst (hybrid) such as "metal nanoparticles – polymer – inorganic carrier". Actually, obtaining of ruthenium AN complex on a mineral carrier and its subsequent polymerization will lead to the formation of polymer-inorganic composite and it consists of a Ru Nano scale particles with 4-8 nm diameter and their 10-20 nm dimensional aggregates.

There are broad diffraction peaks relating to Crystallex Ru^0 in 20 nm areas of the obtained samples radiographs (Fig. 2). A common condition of the diffraction peaks and the expansion line shows the states of ultrafine particles.

Analyzed system shows a sufficiently high activity in a model reaction of cyclohexene hydrogenation. This initial reaction rate on poly $RuAN/SiO_2$ catalyst condition are approximately 2 times more than Ru/C catalyst (Table 2, Fig. 3).

Table 2

The initial rate of cyclohexene hydrogenation reaction (W_o) in the presence of hybrid polymer-immobilized Ru nanoparticles

Таблица 2. **Начальная скорость реакции гидрирования циклогексена (W_o) в присутствии гибридных полимерных иммобилизованных Ru наночастиц**

Sample	Obtaining condition	W_o, mol/l^{-1} sec^{-1}		
		1 cycle	2 cycle	3 cycle
Poly-$RuAN/SiO_2$	FP	22.9	16.7	-
	FP, 100°C	10.8	12.6	10.1
	FP, 120°C	13.4	10.5	11.2
	FP, 150°C	1.1	3.48	5.2
Ru/C		11.6	11.6	

Examined nano composite maintains its activity and re-cyclization, and an immobilized form enables easily to separate it from the reaction mixture and it can be reusable.

Ru nanoparticles formation condition influences on the catalytic properties of the studied nano composite, for example, the use of different FP modes on inert media. The hydrogenation rate of cyclohexene on the Nano composites obtained at high temperatures decreases. It is assumed that the reason of the reaction rate decrease is due to the increase of Ru particles size.

It should be noted that after hydrogenation, the bulk of Ru in poly-RuAN (90%) will have zero valency and its shielding by polymer matrix reduces. The polymer matrix is also subjected to alteration and confirmed by spectrum spreading.

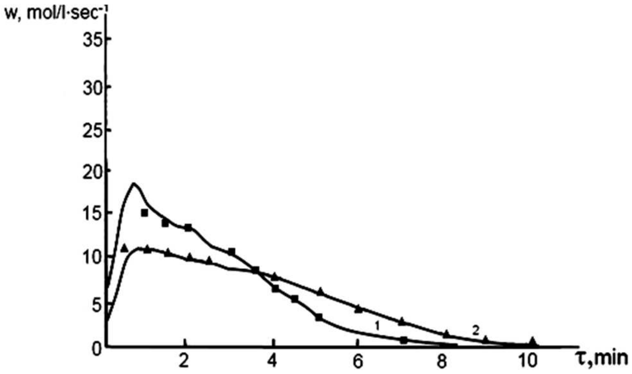

Fig. 3. Kinetic curves of hydrogen absorption at cyclohexene hydrogenation in the presence of poly- Ru AN/SiO_2 (1) and Ru/C (2). Weight of catalyst is 0.05-0.10 g, temperature is 20 °C, H_2 pressure is 0.1 MPa, solvent - isopropyl alcohol, initial amount of cyclohexene is 6.9 mole

Рис. 3. Кинетические кривые поглощения водорода при гибридизации циклогексена в присутствии поли-Ru AN/SiO_2 (1) и Ru/C (2). Вес катализатора 0,05-0,10 г, температура 20 °С, давление водорода 0,1 МПа, растворитель - изопропиловый спирт, исходное количество циклогексена 6,9 моль

CONCLUSION

Thus, the synthesized hydrogenation over of polymer-immobilized Ru nanoparticles shows high activity in cyclohexene hydrogenation reaction and keeps its activity during repeated cycles. The catalytic properties of the Nano composites depend on the conditions of their preparation and it affects the size of the formed Ru nanoparticles.

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