Three-component Au—Chitosan—SiO_2 systems as heterogeneous catalysts for intramolecular cyclization of 2-(2-phenylethynyl)aniline

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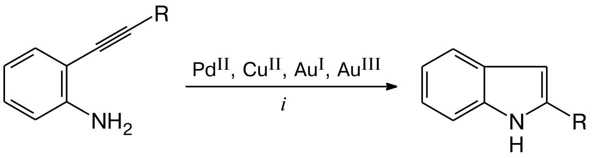
A series of three-component heterogeneous catalysts Au—Ch—SiO_2 with Ch for chitosan was prepared. The size of gold nanoparticles immobilized on the chitosan matrix depends on the method of sample preparation. The particles with the size <3 nm are formed when the preliminary prepared homogeneous Au—Ch complex is supported on SiO_2. The catalysts were tested in the intramolecular cyclization reaction of 2-(2-phenylethynyl)aniline to for 2-phenylindole. The maximum conversion of 2-(2-phenylethynyl)aniline (25% within 35 h) was obtained on the Au(0.4%)—Ch(2.9%)/SiO_2 catalyst.

Key words: catalytic intramolecular hydroamination of 2-(2-phenylethynyl)aniline, catalysts based on gold nanoparticles, chitosan.

Reactions of intramolecular cyclization of 2-alkynylanilines are among the most promising methods for the preparation of indoles, which are components of many natural and synthetic substances with biological activity.[1] These reactions are usually catalyzed by the Pd^{II} and Cu^{II} compounds.[2,3] The possibility that this reaction occurs in the presence of the Au^{III} salts or Au^{I} compounds has recently been shown (Scheme 1). However, only homogeneous catalytic systems were used in the published works.[4—7]

Scheme 1



i. CH_2Cl_2/HCl_{aq}, EtOH, EtOH/H_2O, ~20 °C.

R = Ar, Alk, vinyl, H

Data on the application of gold nanoparticles as heterogeneous catalysts of intramolecular cyclization of various ethynylanilines are very restricted.[8,9]

It is known that the heterogeneous gold-containing catalysts are characterized by size effects, since their activity depends on the particle size. It is very important to prevent enlargement of small particles in these catalytic systems. One of the approaches frequently used to prevent gold nanoparticle agglomeration is their immobilization into matrices of various polymers.[10]

Chitosan (poly(1—4)-*N*-acetyl-β-D-glucosamine) is linear polysaccharide with polymer chain built of β-1,4-bonded glucosamine residues and minor amounts of *N*-acetylglucosamine (chitin) units. The primary and secondary structures of this polysaccharide resemble the cellulose structure. Chitosan is the product of the deacetylation of natural biopolymer chitin, which is the major component of shells of various Crustacea. Therefore, chitosan is the second in abundance in nature after cellulose.

Since a monomeric unit of chitosan contains nitrogen- and oxygen-containing functional groups, chitosan exhibits a unique sorption ability toward many metal ions and even metal atoms. The polymer matrix of chitosan can irreversibly bind various ions and for this reason it attracts attention mainly as an efficient system of removal of heavy metal cations from dilute aqueous solutions. The studies of the sorption properties of the gold—chitosan complexes have been started fairly long ago,[11,12] and the possibilities of applying the chitosan polymer matrix for the stabilization of gold nanoparticles and using these systems in heterogeneous catalysis were considered.[9]

The use of chitosan as a support in catalysis is fraught with problems. The first problem is a small specific surface area of chitosan, and the second problem is insufficient

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resistance to attrition. One of the methods for surmounting these problems is the preparation of three-component systems metal—chitosan—oxide support (the latter should have a sufficient surface area and relatively high mechanical strength[13—16]).

The purpose of this work is the development of active three-component catalysts Au—Ch—SiO_2 (Ch is chitosan) for the intramolecular cyclization of 2-(2-phenylethynyl)aniline to 2-phenylindole.

Experimental

Commercial reagents 2-(2-phenylethynyl)aniline (OakwoodChemical, 99+%), chloroauric acid, sodium chloroaurate, 2-phenylindole (95%) (Sigma—Aldrich), ethanol, and glacial acetic acid (reagent grade, Reakhim) were used as received.

Chitosan was obtained from crab shells (South Korea, molecular weight 100 000—150 000, degree of deacetylation of amino groups 70%, moisture content 3 wt.%) and was used without additional purification.

Silica gel KCK (S_{BET} = 330 $m^2 g^{-1}$ (GOST 3956-76, Karpov Chemical Plant, Mendeleevsk, Russia) and silica gel KCC No. 3 (S_{BET} = 450 $m^2 g^{-1}$ (GOST 3956-76, Reakhim) were used as supports. The silica gels were multiply washed with dilute HCl to remove iron impurities.

The three-component catalysts were obtained by three different methods: samples **I** and **II** were prepared by depositing gold and chitoses on silica gel according to the published procedure,[9] sample **III** was obtained by depositing gold on silica gel that was impregnated several times with chitosan, and samples **IV** and **V** were prepared by depositing the pre-synthesized homogeneous Au—Ch complex on silica gel. The calculated composition of the samples and their designations are presented in Table 1.

To obtain sample **III**, silica gel KCK (fraction 0.85—0.1 mm, humidity ratio 0.4 mL g^{-1}) was three times impregnated with a chitosan solution in 1.5% AcOH (2.2 g of chitosan in 150 mL of the acid) using the incipient wetness impregnation method. After each impregnation, silica gel with supported chitosan was placed in a 0.5 *M* NaOH solution and kept for 3 h, after which the impregnated silica gel was washed to a neutral pH with distilled water and filtered. The obtained white powder was dried for 1 h at 80 °C. The amount of chitosan supported on silica gel was determined from an increase in the weight of the initial silica gel. To deposite gold on the Ch—SiO_2 support, the latter was refluxed for 6 h in an ethanolic solution of $NaAuCl_4$ with a reflux condenser. The progress of the reaction was followed by the decolorization of an ethanolic solution of the gold-containing precursor. After reflux, the precipitate was filtered, washed with EtOH, and dried in air for 24 h.

Table 1. Composition of the three-component Au—Ch—SiO_2 catalysts

Catalyst	Trade mark of silica gel	Composition of three-component catalyst
I*	KCC No. 3	Au(3.5%)—Ch(18%)—SiO_2
II	KCC No. 3	Au(4%)/Ch(29%)—SiO_2
III	KCK	Au(0.8%)/Ch(5.9%)—SiO_2
IV	KCK	Au(0.4%)—Ch(2.9%)/SiO_2
V	KCC No. 3	Au(0.6%)—Ch(4.3%)/SiO_2

* According to the ICP-OES data, the gold content in the catalyst is 2.78 wt.%.

To obtain samples **IV** and **V**, the homogeneous Au—Ch complex was pre-synthesized. The calculated amount of the gold-containing precursor corresponding to the ion-exchange capacity of chitosan[17] was introduced into a chitosan solution in 1.5% AcOH. The suspension was stirred to the complete dissolution of sodium chloroaurate. The obtained Au—Ch complex was immobilized in silica gel by the incipient wetness impregnation method. After impregnation, the catalysts were kept for 16 h in a 0.5 *M* NaOH solution. The catalyst was filtered and multiply washed with distilled water to a neutral pH. The prepared catalysts were dried in air for 24 h.

Intramolecular hydroamination was carried out in a round-bottom flask with a reflux condenser. In a standard experiment, the reaction mixture was stirred at ~20 °C in argon. The molar ratio substrate : catalyst was 20 : 1, and ethanol (3—6 mL) served as a solvent.

The progress of the reaction was monitored using GLC (KristaLyuks 4000 M chromatograph, capillary column OV 1 with a length of 30 m, flame-ionization detector, helium as a carrier gas). The temperatures of the evaporator, detector, and column (isotherm) were 240, 240, and 210 °C, respectively. The total analysis time was 11 min. The sensitivity coefficients of the detector to the components of the reaction mixture determined by calibration mixtures were 1.1 and 0.9 for 2-(2-phenylethynyl)aniline and 2-phenylindole, respectively.

Diffuse reflectance infrared Fourier transform spectra (DRIFTS) were recorded at ~20 °C on a Nicolet 460 Protégé spectrometer with the diffuse reflectance attachment. Catalyst samples were placed in ampules with a CaF_2 window. A CaF_2 powder was used as a reference sample. To obtained a satisfactory signal to noise ratio, 500 spectra were accumulated. IR spectra were measured in a frequency range of 400—6000 cm^{-1} with a resolution of 4 cm^{-1}. Carbon monoxide served as a molecular test, which was adsorbed at ~20 °C and at an equilibrium pressure of 15 Torr.

The phase composition of the catalyst samples was determined by X-ray diffraction analysis (XRD). The XRD patterns were detected on a DRON-2 instrument in Ni-filtered Cu-Kα radiation (λ = 0.1542 nm) in the step scan mode (with an increment of 0.02°) in the range 2θ = 10—80°. The crystalline phases were identified by comparing of the position and intensity of peaks in the X-ray pattern with ICDD references.

The photoelectron (XPS) spectra were recorded on a SES 2002 photoelectron spectrometer with a hemispherical analyzer (Gammadata-Scienta, monochromatic Al-Kα radiation, $h\nu$ = = 1486.6 eV). The main chamber was evacuated to $4 \cdot 10^{-10}$ Torr. The measurements were carried out at the energy of the analyzer fixed at a value of 200 eV that gives the resulting absolute resolution equal to 0.25 eV. The charge of the sample surface was compensated by a low-energy electron beam. In the further processing, the Si2p binding energy (102.7 eV) was used as a reference to additionally correct the XPS peak positions. The binding energy (BE) scale was pre-calibrated by the position of peaks of the framework levels $Au4f_{7/2}$ (84.0 eV), $Cu2p_{3/2}$ (932.7 eV), and $Ag3d_{5/2}$ (368.3 eV). The surface atomic ratios of elements were calculated from the line intensities and corresponding photoionization cross sections.[18]

The gold content in the catalysts was determined by Inductively coupled plasma/optical emission atomic spectroscopy (ICP-OES) on an optical emission spectrometer (Unicam, PU700).

Results and Discussion

The XRD study of the obtained catalysts shows that the size of gold nanoparticles immobilized in the chitosan matrix depends on the preparation method (Table 2). The size of gold particles in samples **IV** and **V** prepared by the deposition of the pre-formed homogeneous Au—Ch complex on silica gel does not reach 3 nm. The synthesis according to a described procedure[9] gives rather large gold particles: 14—15 nm in size (samples **I** and **II**). The particles 26 nm in size are formed by gold immobilization on the Ch—SiO_2 support (sample **III**).

The shape of the XPS spectrum of the Au(3.5%)/Ch—SiO_2 sample (Fig. 1) resembles that of the spectrum characteristic of silica, since it contains high-intensity peaks from C1s and framework levels Si2p, Si2s, and O1s, as well as low-intensity Au4f doublets. The lines of the N1s framework level are also well seen in the spectra.

The position of the lines of the $Au4f_{7/2}$ framework levels of the Au(3.5%)/Ch—SiO_2 sample (Fig. 2) is insignificantly shifted toward higher BE compared to the BE corresponding to the metallic state of gold (84.0 eV). In addition, the components of the Au4f doublet in the spectrum of this sample have a larger FWHH (full width at half-height) compared to the spectra of two other samples, indicating an additional state of gold. In fact, the decomposition of the spectrum into components (Fig. 3) in the form of the Voigt function (deconvolution of the Gaussian and Lorentzian functions) gives two doublets with the intensity ratio 8.2 : 1. A more strong $Au4f_{7/2}$ line with a BE of 84.0 eV corresponds to the metallic state of gold, whereas the component with weaker intensity of the doublet has the BE equal to 85.7 eV, which is close to the value determined earlier[19] for the organic gold complexes.

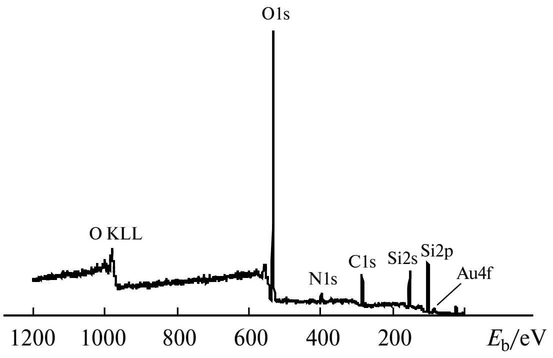


Fig. 1. XPS review spectrum of the Au(3.5%)/Ch—SiO_2 sample; E_b is the binding energy.

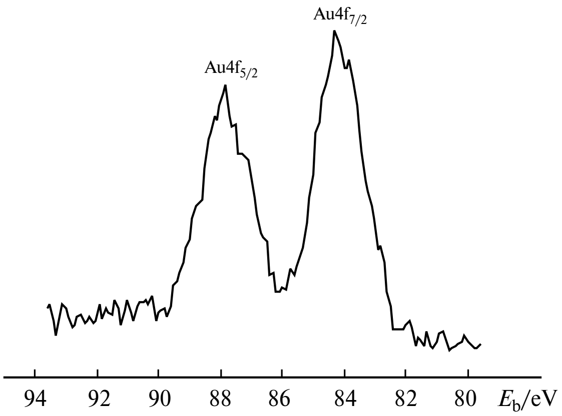


Fig. 2. XPS Au4f spectrum.

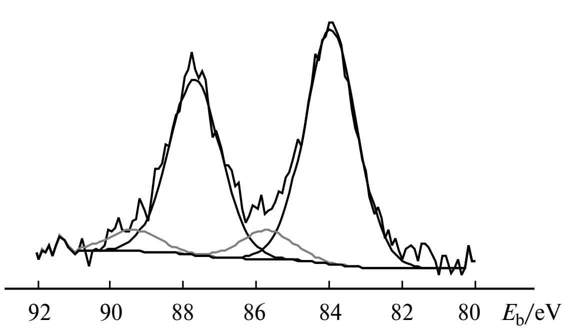


Fig. 3. Deconvolution of the photoelectron Au4f spectrum of the Au(3.5%)/Ch—SiO_2 sample.

The initial catalysts **I**, **III**, **IV**, and **V** and the same catalysts after the catalytic reaction were studied by the DRIFTS method. Prior to CO feeding, the samples were treated *in vacuo* at 20 °C for 3 h to remove physically adsorbed gases and water. The adsorption of CO was carried out at ~20 °C and at an equilibrium pressure of 15 Torr. The obtained results are presented in Table 2.

When using carbon monoxide as a testing molecule to specify the electronic state of gold, it was found that CO was not adsorbed on all initial samples even after prolong (17 h) storage in CO at ~20 °C. Low-intensity bands of CO adsorbed on the Au sites were detected in the spectra of catalysts **III** and **IV** used in catalytic intramolecular cyclization. The intensity of the spectra is very low. After desorption to vacuum at ~20 °C, no band of adsorbed CO was observed in the spectra. The stretching vibration frequencies in CO molecules adsorbed on the Au sites are 2188 and 2172 cm^{-1}. These bands can be assigned to stretching vibrations in CO molecules in the linear carbonyl complexes with gold cations (Au^{n+}). The difference in the vibration frequencies can be related to both different effective charges of the gold cations and their different environments.[20]

Table 2. Sizes of gold particles. character of CO adsorption, and electronic state of gold in the three-component Au—Ch—SiO_2 catalysts obtained by the interaction of $HAuCl_4$ with the NH_2 groups of the support and reduced on reflux of the polymer matrix in EtOH

Catalyst	Size of Au particles/nm (XRD)	Character of CO adsorption according to DRIFTS data	Electronic state of Au (XPS)
I	14	No adsorption is observed	Au^0, Au^+, organic gold complexes
II	15	No adsorption is observed	Au^0
III	26	No adsorption is observed	Au^0
IV*	<3	Low-intensity bands of adsorbed CO	Was not studied
V	<3	Low-intensity bands of adsorbed CO	Was not studied

* Unreduced sample.

Table 3. Results of the intramolecular cyclization of 2-(2-phenylethynyl)aniline on the three-component Au—Ch—SiO_2 catalysts (~20 °C)

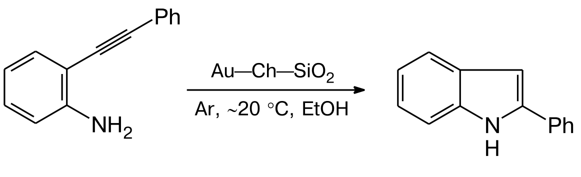
Catalyst	Synthesis time	Conversion of 2-(2-phenylethynyl)aniline (%)	Specific productivity $\cdot 10^3$ /mmole of indole (mmole of Au)$^{-1}$ h^{-1}
I	20	1.0	10
II	84	+8*	2.0
	3.0	4	6
III	85	12.6	30
IV	35.5	25.1	140
V	44.5	13.8	60

* 60 °C.

The results obtained on investigating the catalysts by the DRIFTS methods are presented in Table 2 and supplemented by the XRD and XPS data.

Catalysts **I**—**V** were tested in the intramolecular hydroamination of 2-(2-phenylethynyl)aniline. According to the chromatographic analysis data and the results of preliminary study of the reaction mixtures by ^{1}H and ^{13}C NMR spectroscopy, 2-phenylindole is the only product of the conversion of 2-(2-phenylethynyl)aniline under the studied conditions on all the three-component Au—Ch—SiO_2 catalysts (Scheme 2).

Scheme 2



The obtained results are presented in Table 3.

The maximum conversion of 2-(2-phenylethynyl)aniline achieved on the three-component Au—Ch—SiO_2 systems was obtained with the Au(0.4%)—Ch(2.9%)/SiO_2 catalyst (**IV**) (25% within 35 h).

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