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Gold-Containing Catalysts Based on Mesoporous Metal–Organic Frameworks of the MIL Type for Regioselective Hydroamination Reaction of Phenylacetylene

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Abstract—Catalyst systems based on gold nanoparticles introduced into the matrices of mesoporous metal–organic frameworks of the MIL type based on trivalent metal ions (Al, Fe) manifest activity in the regioselective hydroamination of phenylacetylene with aniline according to the Markovnikov rule. The activity of the synthesized gold-containing systems significantly depends on the nature of organic and inorganic building units, metal ions, and organic linkers, which form the framework, as well as on the catalyst preparation procedure.

Keywords: hydroamination, Markovnikov addition rule, metal–organic frameworks, nanoparticles, catalysis, gold

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INTRODUCTION

In the recent decade, metal–organic frameworks (MOFs) have attracted the attention of researchers as carriers of heterogeneous catalysts [1]. Metal–organic frameworks are a class of ordered zeolite-like materials, the structure of which is formed by inorganic and organic building units, metal ions, and polydentate organic linker molecules bound into a three-dimensional framework by coordination bonds [2]. The unique characteristics of these inorganic–organic materials create conditions for fine tuning and controlling heterogeneous catalyst systems based on them. In particular, a high specific surface area and a high pore volume with uniform size and shape distribution make these systems promising materials for stabilizing active metal nanoparticles that are labile under other conditions [3]. The application of metal–organic frameworks as matrices for the introduction of metal nanoparticles promotes their uniform distribution and guarantee of high dispersity. These characteristics of supported metal nanoparticles create conditions for enhancing the catalytic properties of thereby obtained nanohybrids [4].

It is known that the method of introduction of a metal into porous MOF matrices determines to a significant extent the location and dispersity of the introduced nanoparticles [5]. In turn, these characteristics of heterogeneous systems affect the activity and selectivity of M/MOF nanomaterials. On the other hand, metal–organic frameworks utterly correspond to the task of finding the effect of the method of preparation on the catalytic properties of heterogeneous systems due to a set of characteristics such as the topology and functionality of the network, porosity, and structural properties variable in a wide range. In this connection, the development of simple methods for the immobilization of precious metal nanoparticles in MOF matrices for obtaining active and selective catalyst materials is an important and at the same time unconventional problem.

The aim of this work consisted in the preparation of gold-containing nanomaterials based on metal–organic frameworks (Au/MOF). Special attention was paid to studying the effect of their preparation method on the dispersity and localization of gold nanoparticles in the metal–organic matrices, and, thus, on the catalytic properties of the nanohybrids being formed. In view of the above, Au nanoparticles were introduced into highly porous MOF supports according to two alternative procedures, namely, incipient wetness (dry) impregnation and wet impregnation.

It is known [6] that the catalytic activity of Au nanoparticles depends on their size to a greater extent than in the case of nanoparticles of other metals, e.g.,

Table 1. Metal–organic frameworks of the MIL type—the supports of Au nanoparticles

MIL	Composition	Porous structure	Specific surface area, S_{BET}, m^2/g
MIL-100(Fe)	$Fe_3O(OH)(btc)_2$ btc = benzene-1,3,5-tricarboxylate	"Windows" of 0.55–0.86 nm and voids of 2.5–2.9 nm	1665
NH_2–MIL-101(Al)	$Al_3O(abdc)_3$ abdc = 2-aminobenzene-1,4-dicarboxylate	"Windows" of 1.2–1.6 nm and voids of 2.9–3.4 nm	2100

palladium. In this connection, one of the key problems for gold-containing catalysts is controlling the particle size distribution in the corresponding range. As has been noted above, the use of metal–organic frameworks with a certain topology of the framework structure and high porosity and specific surface area as matrices for the encapsulation of gold nanoparticles makes it possible to solve this problem. From this perspective, an important direction of this research was to reveal the contribution from the characteristics of the metal–organic frameworks (structure, topology) to the stabilization of Au nanoparticles in these matrices and the catalytic properties of the Au/MOF nanohybrids obtained. For this purpose, MIL-100(Fe) and NH_2–MIL-101(Al) mesoporous frameworks based on Fe^{3+} and Al^{3+} ions and benzene-1,3,5-tricarboxylate and 2-aminobenzene-1,4-dicarboxylate linkers, respectively, were used as the carriers of gold nanoparticles (Table 1). These matrices were chosen due to the large size of the pores in the form of nanocavities (2.4–3.4 nm, Table 1). The presence of these voids limited by small "windows" in NH_2–MIL-101(Al) and MIL-100(Fe) matrices makes it possible to provide a limiting effect of the porous structure of the framework with respect of gold nanoparticles.

To increase the efficiency of the metal–support interactions, a NH_2–MIL-101(Al) framework modified by amino groups in the organic linkers, which may promote the stabilization of gold nanoparticles in the pores and prevent their aggregation during and after the catalytic reaction, was chosen. The MIL-100(Fe) framework is of interest due to the coordinatively unsaturated sites, Fe^{3+} ions, which may provide a synergistic effect in combination with Au nanoparticles in the case of using Au/MIL-100(Fe) as a catalyst.

The regioselective hydroamination reaction of phenylacetylene by aniline was chosen for testing the catalytic properties of the Au/MIL obtained nanohybrids. It should be noted that the hydroamination reaction attracts increased attention of researchers as a direct way for forming the C–N bond with the preparation of valuable products and intermediate products of fine chemical synthesis and physiologically active compounds [7]. By now, various heterogeneous and homogenous catalyst systems for carrying out this reaction have been developed [8]; however, published sources contain only sporadic information about hydroamination in the presence of catalysts based on MOF matrices [9].

The synthesized MIL matrices and gold-containing catalysts based on them were characterized by a set of instrumental methods, such as X-ray diffraction (XRD) analysis, diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS), and low-temperature adsorption of nitrogen.

EXPERIMENTAL

Synthesis of MIL Samples and Gold-Containing Catalysts on Their Basis

The samples of MIL-100(Fe) and NH_2–MIL-101(Al) were prepared under solvothermal conditions under autogenous pressure generated by solvent vapors at an elevated temperature in a closed volume.

NH_2–MIL-101(Al) [$Al_3O(abdc)_3$]. The sample was synthesized according to a modified procedure [10]. The synthesis conditions were modified as follows: the reaction temperature (110°C) was decreased in comparison with the published procedure (130°C). The mixture of the reactants $AlCl_3 \cdot 6H_2O$ (0.51 g, 2.11 mmol), 2-aminobenzene-1,4-dicarboxylic acid (0.56 g, 3.09 mmol), and DMF (40 mL) was stirred with a magnetic stirrer until complete dissolution of the reactants and heated in a thermostat (110°C, 72 h). The product was isolated on a centrifuge (4000 rpm), rinsed with DMF (3 × 20 mL), and treated with acetone (3 × 20 mL) followed by ethanol (3 × 20 mL). The yellow crystalline substance was evacuated using an oil pump (1×10^{-3} torr) for 2–4 h (20°C) and then at a gradually increasing temperature: 90°C for 3 h, 120°C for 2 h, and 160°C for 4 h. A finely dispersed yellow powder was obtained after evacuation.

MIL-100(Fe) [$Fe_3O(OH)(btc)_2$]. The sample of MIL-100(Fe) was synthesized under hydrothermal conditions according to a published procedure [11]. Anhydrous iron chloride (0.487 g, 1.0 mmol) and $(CH_3O)_3$btc (0.499 g, 0.66 mmol) were dissolved in 17 mL of distilled water. The resulting solution was placed into a 60-mL Teflon liner that was transferred into a steel autoclave. The autoclave with the reaction mixture was heated in a drying oven at 130°C for 72 h. The precipitate formed was isolated by centrifuging, rinsed with distilled water (3 × 10 mL), and then treated with dehydrated acetone (20 mL) under stirring (24 h). It was further isolated on a centrifuge and dried in vacuum (7 h, 60°C, 10^{-2} torr).

Prior to introducing gold nanoparticles, the samples of mesoporous frameworks were activated in vacuum to remove the "guest" molecules of the reactants and solvent (DMF), captured during the synthesis, from the pores (150°C, 7 h, 10^{-2} torr).

The preparation of catalysts by incipient wetness impregnation. Gold (3.7–5 wt %) was deposited by mixing 1.2 g of a sample of MIL with a solution of $HAuCl_4 \cdot 3H_2O$ (11–13 mg) in absolute ethanol (0.30 mL). The samples containing the gold precursor were dried under reduced pressure (90°C, 5 h) and then subjected to vacuum heat treatment (100°C, 4 h, 10^{-2} torr).

Wet impregnation. The activated support (100 mg) was mixed with a solution of $HAuCl_4 \cdot 3H_2O$ (50 mg) in deionized water (5 mL) at 50°C (24 h).

Gold nanoparticles introduced into the MIL-100(Fe) and NH_2–MIL-101(Al) matrices were obtained by reduction with a sodium borohydride solution in ethanol (22°C). Then, the gold-containing hybrid nanomaterials based on the MIL matrices (Au/MIL) were dried in a vacuum (150°C, 5 h, 10^{-2} torr).

Instrumental Characterization of MIL Samples and Au/MIL Catalysts Based on Them

X-ray diffraction analysis. To confirm the phase composition of the samples, X-ray diffraction measurements were performed at room temperature on an EMPYREAN powder diffractometer (PANalytical, the Netherlands) (nickel-filtered CuK_α radiation, an X'Celerator linear detector, Bragg–Brentano geometry) in the 2θ angle range of 7°–40° .

Infrared (IR) spectra of the samples were obtained on a Nicolet Protege 460 spectrometer by the diffuse scattering procedure. The Fourier-transform IR spectra were recorded at a resolution of 2 cm^{-1}. The data acquisition and processing were performed using the OMNIC software package. The adsorption of CO (10 torr) was carried out at room temperature followed by its desorption in a vacuum.

Physical adsorption of nitrogen. The porous structure and surface area of the synthesized materials were characterized using a Micromeritics ASAP-2020-Plus instrument by volumetric measurement of nitrogen adsorption; the parameters of the porous structure were calculated by the Brunauer–Emmett–Teller (BET) equation. After degassing at 150°C in a vacuum, the adsorption of nitrogen on the sample was measured at −196°C. Different gas pressures were used to obtain the nitrogen adsorption isotherm. The analysis was performed at a relative pressure of nitrogen N_2 P/P_0 in the range of 0.01 to 0.99.

Catalytic Testing Experiments

A reaction mixture containing a catalyst (0.1 g, 0.05–2.5% mmol metal), phenylacetylene (1 mmol), aniline (1 mmol), toluene (1 mL), and undecane (a chromatographic standard, 0.07 mL, 0.3 mmol) was stirred in a glass reactor with a magnetic stirrer in an air atmosphere (110°C, 8–24 h).

The composition of the reaction solution was studied by gas–liquid chromatography (GLC) (Kristallyuks chromatograph equipped with FID) on a capillary column (OV-1 phase, 25 m) under programmed heating (100–170°C).

Recycling experiments. After carrying out the reaction, the catalyst (5%Au/NH_2–MIL-101(Al)) was separated by centrifugation, rinsed with toluene (3 × 1 mL), refluxed in 1 mL of toluene, and then the catalyst was repeatedly isolated by centrifugation and reused under the same conditions of the catalytic reaction.

RESULTS AND DISCUSSION

The samples of MIL synthesized under solvothermal conditions are distinguished by a high specific surface area, the value of which coincides with the published data [10, 11] (Table 1).

Gold nanoparticles were introduced into the matrices of the mesoporous MIL structures by the postsynthesis modification of the preliminarily synthesized metal–organic frameworks. According to the published data, the deposition of a metal by wet impregnation leads to the formation of particles inside the support pores, whereas the nanoparticles are mainly localized on the support surface in the case of incipient wetness impregnation [3].

Instrumental Studies of Mesoporous MIL-100(Fe) and NH_2–MIL-101(Al) Frameworks and Au/MIL Nanomaterials Based on Them

The morphology of the synthesized NH_2–MIL-101(Al) sample was identified by comparing the experimental X-ray diffraction pattern with the theoretical X-ray diffraction pattern by the known crystal lattice parameters (cubic cell Fd-3m, a = 87.536(27) Å [12] (Fig. 1)).

The morphology of the obtained sample of MIL-100(Fe) was identified by comparing the experimental X-ray diffraction pattern with the theoretical X-ray diffraction pattern by the known crystal lattice param-

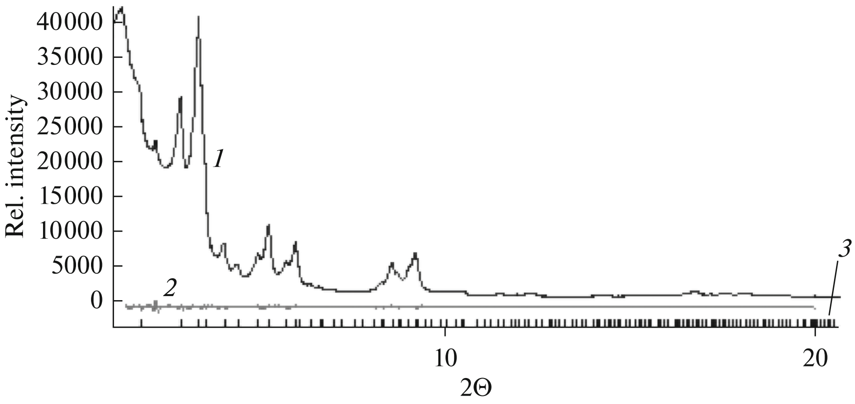


Fig. 1. (*1*) X-ray diffraction pattern of the synthesized sample of NH_2–MIL-101(Al). (*3*) Calculated X-ray diffraction pattern. (*2*) Difference curve on the structure refinement.

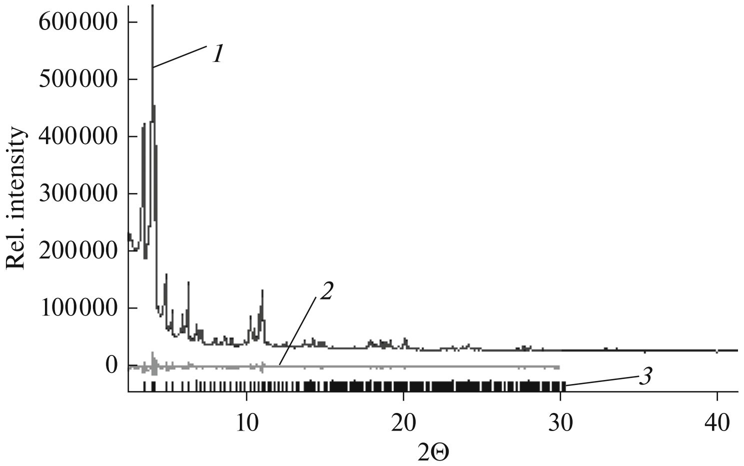


Fig. 2. (*1*) X-ray diffraction pattern of the synthesized sample of MIL-100(Fe). (*3*) Calculated X-ray diffraction pattern. (*2*) Difference curve on the structure refinement.

eters (cubic cell Fd-3m, $a = 72.1$ Å, $V = 388000$ Å [11] (Fig. 2)).

The XRD study of the obtained Au/MIL nanohybrids indicate that the introduction of gold nanoparticles preserves their crystal structure (Fig. 3a). In the case of the samples prepared by incipient wetness impregnation, there is the formation of large (up to ~25 nm) gold nanoparticles on the surface of the MIL supports (Fig. 3b). Probably, in the near-surface layers of the metal–organic matrix, its limiting effect in relation to gold nanoparticles is not as pronounced as in its bulk.

The electronic state of the gold particles localized in the NH_2–MIL-101(Al) mesoporous matrix was studied by IR spectroscopy of adsorbed CO as a probe molecule The study of the 5%Au/NH_2–MIL-101(Al) nanohybrid prepared by impregnation in a solvent excess showed that gold in the oxidized state was present in the form of Au^{n+} particles on the amine-modified support (Fig. 4).

Probably, the presence of the functional amino group in the 2-aminobenzene-1,4-dicarboxylate linker of the mesoporous support stabilizes the charged Au^{n+} particles in this case, thereby preventing their further reduction. In addition, the specific topology of the framework structure, the presence of large voids limited by small "windows" (see Table 1), in combination with the method of preparation of the 5%Au/NH_2–MIL-101(Al) nanohybrid by wet impregnation promotes the predominant localization of the gold particles in the volume of the metal–organic matrix.

Phenylacetylene Hydroamination by Aniline over Au/MIL Nanohybrids

The synthesized Au/MIL nanohybrids demonstrate a quite high activity in the regioselective hydroamination of phenylacetylene by aniline according to the Markovnikov rule (Scheme 1).

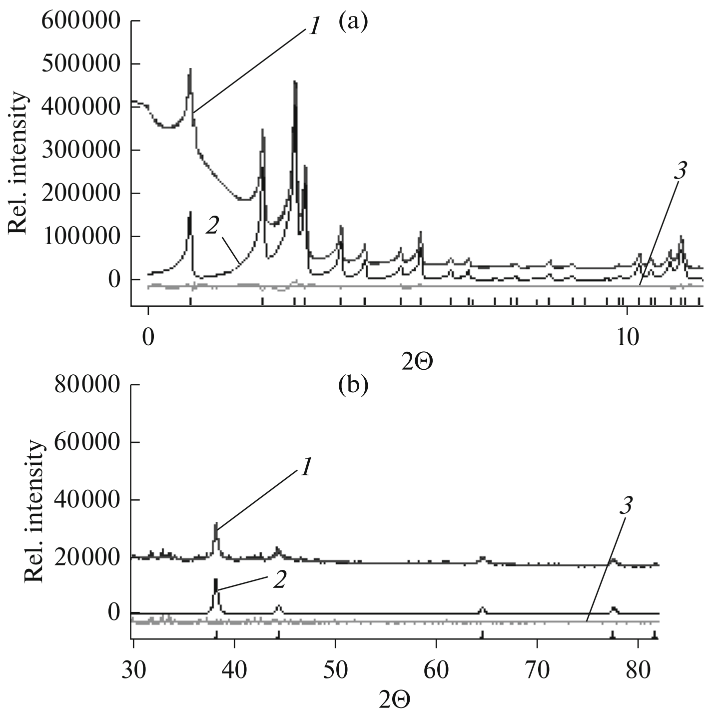


Fig. 3. (a) X-ray diffraction patterns of an Au/MIL-100(Fe) gold-containing nanohybrid in the region of small angles: (*1*) experimental and (*2*) theoretical. (*3*) Difference curve on the structure refinement. (b) X-ray diffraction patterns of an Au/MIL-100(Fe) gold-containing nanohybrid in the region of high angles: (*1*) experimental and (*2*) theoretical. (*3*) Difference curve on the structure refinement. The average diameter of the gold nanoparticles localized on the surface of MIL-100(Fe) is ~25 nm.

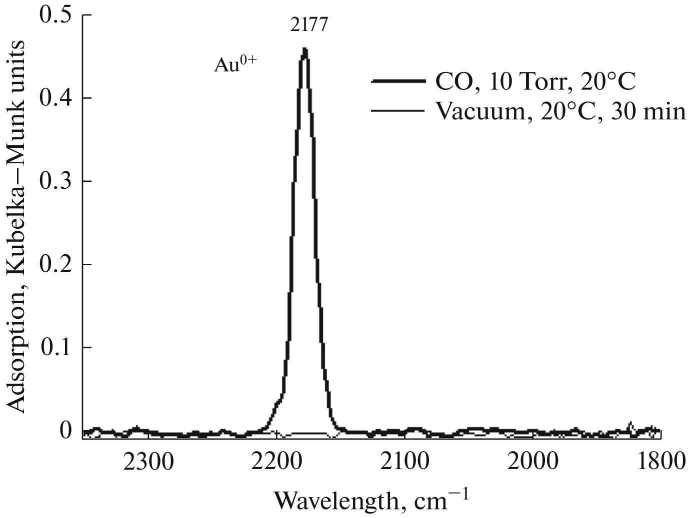
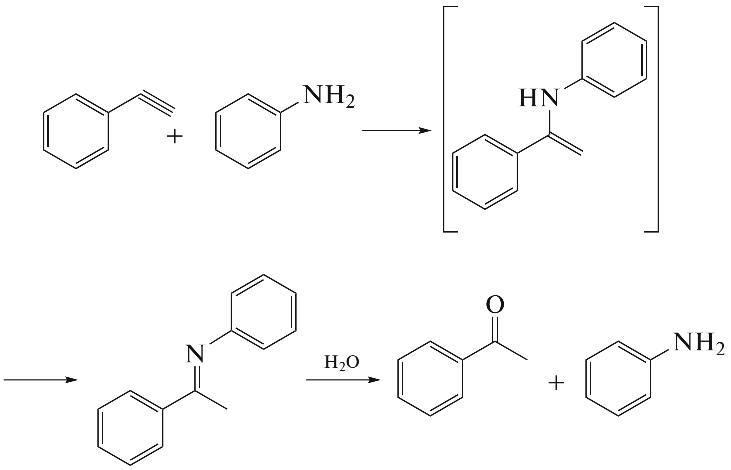


Fig. 4. Spectrum of CO adsorbed on the 5%Au/NH_2–MIL-101(Al) gold-containing nanohybrid prepared by the impregnation in an excess of a solvent.



Scheme 1. Hydroamination of phenylacetylene by aniline.

Depending on the nature of the metal–organic support and the method for preparing the gold-containing nanocatalyst, almost quantitative conversion is observed over 19–30 h (Table 2). The activity of the synthesized Au/MIL catalyst systems is determined to a significant extent by the nature of the organic linker and inorganic building unit (metal ion) in the composition of the framework, as well as by the framework preparation procedure. The highest rate of hydroamination (expressed in TOF) is achieved over gold-containing MIL-100(Fe) obtained by dry impregnation. This method of preparation promotes the accessibility of the active sites, Au nanoparticles, localized near the surface of the MIL-100(Fe) framework, for the substrates phenylacetylene and aniline. In addition, in the case of the MIL-100(Fe) matrix based on Fe^{3+} ions, a synergistic effect of the second metal (iron) that increases the activity of the Au/MIL-100(Fe) nanohybrid and yield of the imine (hydroamination product) is possible.

The lowest activity and yield of the target product (imine) are observed for the gold-containing catalyst based on the NH_2–MIL-101(Al) framework prepared by wet impregnation. When carrying out the hydroamination over this sample (5%Au/NH_2–MIL-101(Al)*), the yield of the target product and the conversion of the reactants are lower than those in the presence of the 5%Au/NH_2–MIL-101(Al) nanocomposite obtained by dry impregnation. Apparently, the amino groups in the organic linkers of the NH_2–MIL-101(Al) framework promote the stabilization of the active sites in the bulk of the metal–organic matrix. The method of preparation by wet impregnation has an additional effect in relation to the immobilization of Au nanoparticles in the intracrystalline space of the framework. Such a specific location of the active sites inside the pores of the support complicates the mass transport (internal diffusion) of the bulky molecules of the reactants and products to them.

All the synthesized Au/MIL catalytic nanomaterials demonstrate high imine (target product) selectivity in the hydroamination reaction (Table 2). The selectivity of gold-containing catalyst systems depends on both the method of introduction of Au nanoparticles and the framework functionality. In particular, the highest imine selectivity of the reaction of ~95–99% is achieved in the case of the 5%Au/NH_2–MIL-101(Al) catalyst system prepared by wet impregnation. On the opposite, the imine selectivity of hydroamination is noticeably lower (30.4%) over the 3.7%Au/MIL-100(Fe) nanohybrid based on the MIL-100(Fe) framework. The increased selectivity of the Au/NH_2–MIL-101(Al) nanohybrid is probably due to the effect of the amino group in the organic linker. This functional group may facilitate the uniform distribution of

Table 2. Hydroamination of phenylacetylene over Au/MIL nanohybrids. Catalyst (0.1 g, 2.5% mmol metal), phenylacetylene (1 mmol), aniline (1 mmol), T_{react} = 110°C

Nanohybrid	TOF × 10^3, s^{-1}	Reaction time, h	Conversion, %	Yield of imine, %	Yield of ketone, %	Imine selectivity, %
5%Au/NH_2–MIL-101(Al)*	0.3	81.0	52.4	41.3	11.1	78.8
5%Au/NH_2–MIL-101(Al)	2.9	22.0	75.0	75.0	0.0	99.0
3.7%Au/MIL-100(Fe)	10.6	20.0	99.0	30.0	69.0	30.4

* The catalyst is synthesized by wet impregnation.

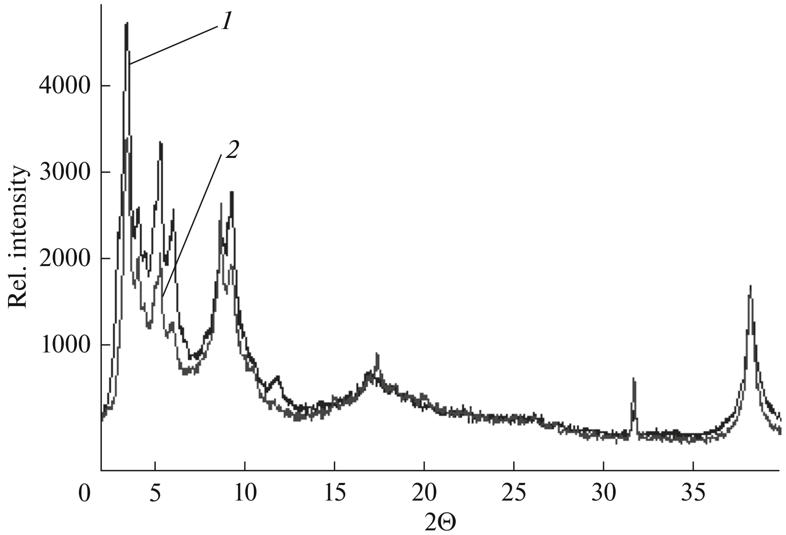


Fig. 5. X-ray diffraction patterns of a 5%Au/NH_2–MIL-101(Al) nanohybrid (*1*) before and (*2*) after carrying out the catalytic reaction.

gold particles in the bulk of the metal–organic matrix and thus provide the uniformity of the active sites.

Catalytic Stability of the 5%Au/NH_2–MIL-101(Al) Nanohybrid

The stability of the 5%Au/NH_2–MIL-101(Al) heterogeneous system was studied in three catalytic cycles of hydroamination of phenylacetylene with aniline. It should be noted that the difference in the values of aniline conversion in the first catalytic cycle (Table 3) in comparison with the results presented in Table 2 is apparently explained by the different concentrations of the catalyst (5%Au/NH_2–MIL-101(Al)) in both cases. Indeed, we earlier showed that the catalyst concentration in the reaction mixture should be 2.5 mmol % Au under the optimum conditions. It is seen from Table 3 that the conversion of aniline decreased by 50% in the third catalytic cycle. This phenomenon may be associated with the increased adsorption of the unreacted aniline and the product imine in the support pores despite the treatment of the catalyst with toluene after the completion of the reaction. The imine selectivity decreases in the second and third catalytic cycles. Possibly, the partial shielding of the amino groups in the organic linkers of the NH_2–MIL-101(Al) matrix by the products, which, in turn, leads to a change in the microenvironment of the active sites (gold nanoparticles) in the pores of the metal–organic support, makes a certain contribution to the decline in the selectivity.

The assumption that the decrease in the conversion of the heterogeneous system under study in the catalytic cycles is associated with the blocking of active sites in the support pores, rather than with the decrease in the concentration of the active phase, is in agreement with the results of the XRD study of the morphological stability of the 5%Au/NH_2–MIL-101(Al) nanohybrid under the conditions of the hydroamination reaction. Comparing the X-ray diffraction patterns of this heterogeneous system before and after catalysis (Fig. 5) shows the preservation of the morphology of the NH_2–MIL-101(Al) metal–organic framework. In addition, the intensity of the reflection at a high angle of ~38°, which corresponds to gold nanoparticles, remains unchanged after carrying out the phenylacetylene hydroamination by aniline over 5%Au/NH_2–MIL-101(Al). This indicates the absence of the undesired “leaching” of the active phase under these conditions.

The obtained data on the reuse of the 5%Au/NH_2–MIL-101(Al) catalyst system indicate the need for further optimization of the experimental conditions of the catalytic hydroamination reaction and regeneration of the Au/MIL heterogeneous systems, first of all, provision of the conditions for the effective desorption of the reaction products from the pores of the metal–organic matrices.

In summary, the regioselective hydroamination of phenylacetylene with aniline was carried out in the presence of Au/MIL gold-containing hybrid nanomaterials for the first time. The activity and selectivity of the gold nanoparticles fixed in the matrices of the mesoporous metal–organic frameworks in the reaction under study substantially depend on the method of preparation of the gold-containing nanocatalysts, as well as on the nature of the metal–organic framework including the inorganic building units (metal ions) and on the functionality of pore walls. The XRD data indicate the retention of the morphology of the Au/NH_2–MIL-101(Al) nanohybrid after the hydroamination reaction. The highest rate of hydroamination of phenylacetylene by aniline is achieved in the case of using the Au-containing MIL-100(Fe) nanomaterial obtained by incipient wetness impregnation. Conversely, the Au/NH_2–MIL-101(Al) hybrid nanomaterials exhibit increased selectivity in comparison with the Au/MIL-100(Fe) nanocatalyst. Therefore, the use of Au/MIL nanohybrids makes it possible to control their catalytic properties in the practically important reaction under study.

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