Incorporation of carbon dioxide into molecules of acetylene hydrocarbons on heterogeneous Ag-containing catalysts

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The reaction between 2-(2-phenylethynyl)aniline and carbon dioxide on heterogeneous Ag-containing catalysts can lead either to benzoxazine-2-one or to 4-hydroxyquinoline-2(1*H*)-one, depending on the reaction conditions (nature of the base, CO_2 pressure). The structures of the products were confirmed by ^1H and ^{13}C NMR spectroscopy. The maximum yield of the products (60 and 30% for benzoxazine-2-one and 4-hydroxyquinolin-2(1*H*)-one, respectively) is achieved on the catalyst Ag(1%)/γ-Al_2O_3(F). According to the results of physicochemical studies, the high activity of the catalysts in the reactions proceeding *via* triple bond activation results from the combination of three factors. First, the catalyst contains metallic silver particles with the size >2 nm; second, metallic silver particles coexist with silver cations; and third, strong acid sites are present on the support surface.

Key words: carbon dioxide, heterogeneous Ag-containing catalysts, alkyne compounds, benzoxazines, hydroxoquinolines.

It is known that carbon dioxide is a cheap renewable source of C_1. The use of carbon dioxide in chemical syntheses does not presently exceed 1% of the volume of consumable CO_2. Therefore, the development of new catalytic systems that make it possible to involve an inert molecule of carbon dioxide into chemical reactions occurring under mild conditions and providing valuable polyfunctional organic compounds for fine synthesis and pharmacology is an urgent task.[1,2]

The use of toxic and expensive reagents can be avoided using these processes. Silver salts act as π-Lewis acids capable of activating the triple bond in the substrate molecule in the presence of organic bases, for example, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). These salts are efficient catalysts for the reactions of carbon dioxide with propargyl alcohols and propargylamines occurring with the formation of the corresponding cyclic carbonates and oxazolidinones.[3—5]

Another example of the reactions between alkynes and CO_2 catalyzed by silver salts and base is the direct carbonylation to form propiolic acids, valuable polyfunctional compounds widely used in fine synthesis.[6,7]

The reactions of CO_2 with various alkylanilines also catalyzed by the silver salts in the presence of organic bases produce substances with a wide range of biological activity, such as benzoxazin-2-one[8,9] or 4-hydroxoquinoline derivatives.[10]

The purpose of this work is to search for a simple and efficient heterogeneous catalytic system active in the reactions of CO_2 with alkylanilines, in particular, with 2-(2-phenylethynyl)aniline (**1**). This reaction of carbon dioxide results in its incorporation into the substrate molecule to form polyfunctional heterocyclic compounds.

Experimental

The chemicals used in this study were 2-(2-phenylethynyl)aniline (**1**, Oakwood Chemical, 99+%), 3-aminopropyltriethoxysilane (APTES, 99%), 2-phenylindole (95%), DBU (90%), DABCO (diazabicyclo[2.2.2]octane, 98%, Sigma—Aldrich), sodium tetrahydroborate (+98%), *n*-hexane (99%, Acros Organics), DMSO, ethyl acetate, cesium hydroxide, ammonium carbonate, silver nitrate, copper(I) iodide (reagent grade), carbon dioxide (special purity grade, Reakhim). They were used without further purification. Silica gel L5/40 (LA CHEMA) and plates for thin-layer chromatography (Kavalier, Czechoslovakia) were used as received.

The following supports were used for the preparation of the heterogeneous catalysts: zeolite H-Beta (CP 7119), mesoporous silicate material MCM-41, γ-Al_2O_3(F) (3.5 wt.% fluorine), SiO_2 KCC No. 3 (Reakhim), TiO_2 (Aerolist 7709 Rutile, Degussa), and WO_3(18%)—ZrO_2 (Saint-Gobain).

Fluorinated alumina was prepared by treating γ-Al_2O_3 (La Roche) with a solution of ammonium fluoride followed by drying and heating for 2 h in air at 550 °C.

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For surface modification with amino groups, mesoporous silicate MCM-41 was pre-treated for 3 h in a dry air flow at 550 °C (S_{BET} = 896 m^2 g^{-1}) and then refluxed for 24 h in toluene with APTES excess in an argon atmosphere. The support was filtered, washed with toluene and diethyl ether from APTES residues, and dried *in vacuo*. The modified support was designated as APTES—MCM-41.

The characteristics of the used supports and conditions of their precalcination are presented in Table 1.

The heterogeneous catalysts were prepared by the incipient wetness impregnation method.

To reduce the samples with supported silver nitrate, they were treated in flowing hydrogen. The temperature was increased from room temperature to 450 °C with a heating rate of 4 °C min. The samples were then cooled to ~20 °C and purged with Ar for 15 min. The Ag(1%)/APTES—MCM-41 sample was reduced by the treatment with an aqueous solution of sodium borohydride (1.2 moles of $NaBH_4$ (mole of Ag)$^{-1}$). After reduction, the catalysts were washed with water to remove sodium borohydride excess and dried in air for 24 h.

Cesium carbonate Cs_2CO_3 was synthesized by the reaction of cesium hydroxide with ammonium carbonate.

(*Z*)-4-Benzylidene-1,4-hydroxo-2*H*-3,1-benzoxazin-2-one (2). The catalyst (0.0125 mmole of Ag), DABCO (0.2 equiv.), compound **1** (0.125 mmol), and anhydrous DMSO (1 mL) were consequently introduced into a pre-dried autoclave equipped with a stirrer. The autoclave was closed and purged with CO_2 three times, after which CO_2 was fed and an operating pressure was established. The reaction mixture was stirred for 24 h at ~20 °C and $P(CO_2)$ = 10 atm. After the reaction, the autoclave was cooled in an ice-cold bath and the CO_2 pressure was slowly released. Benzoxazin-2-one **2** was isolated from the reaction solution using column liquid chromatography on silica gel L5/40μ. An *n*-hexane—ethyl acetate (2 : 1) mixture served as an eluent. TLC was used for express analysis of the reaction mixture and fractions collected from the column. The fractions containing the product were combined, and the solvent was pumped out under reduced pressure to obtain benzoxazin-2-one **2** as dry white crystals. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 6.26 (s, 1 H); 6.88 (d, 1 H, J = 8.1 Hz); 7.11 (t, 1 H, J = 7.6 Hz); 7.28—7.41 (m, 4 H); 7.59 (d, 1 H, J = 7.9 Hz); 7.80 (d, 2 H, J = 7.6 Hz); 8.72 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 105.82 (C(1)); 114.90 (C(2)); 116.05 (C(3)); 122.98 (C(4)); 124.21 (C(5)); 127.29 (C(6)); 128.54 (C(7), C(8)); 129.25 (C(9), C(10)); 130.36 (C(11)); 133.67 (C(12)); 134.03 (C(13)); 144.91 (C(14)); 148.57 (C(15)).

Table 1. Characteristics of the supports and conditions of their preliminary thermal treatment

Support	T^a/°C	τ^b/h	S_{BET}/m^2 g^{-1}
γ-Al_2O_3	600	2	140—160
SiO_2 KCC No. 3	260	8	450
TiO_2	550	2	15
Al_2O_3(F)	550	2	120
MCM-41	550	3	896
W—ZrO_2	650	2	120

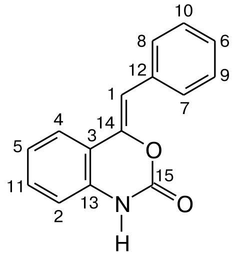
[a] Temperature of thermal treatment.

[b] Duration of thermal treatment.

4-Hydroxy-3-phenylquinolin-2(1*H*)-one (3). The reaction was carried out in a temperature-controlled reactor with a jacket, and CO_2 was introduced into the reactor through a needle inserted into a bottom sampler. The reactor was loaded with compound **1** (0.3 mmol), Ag (0.03 mmol), DBU (0.3 mmol), and DMSO (2 mL). The mixture was stirred for 24 h at 60 °C. To isolate the product, the reaction mixture was filtered and extracted with 1 *M* NaOH (3×4 mL). The aqueous layer was acidified with a solution of 2 *M* HCl to the neutral pH and extracted with EtOAc (5×15 mL). The organic layer was collected, washed with a solution of 2 *M* HCl (2×80 mL), dried over Na_2SO_4, and filtered. The solvent was removed on a rotary evaporator (T = 35 °C, P = 60 mbar) to obtain 4-hydroxyquinolin-2(1*H*)-one **2** as dry white crystals. ^{1}H NMR (400 MHz, $CDCl_3$), δ: 4.37 (s, 2 H); 6.78 (dd, 2 H, J_1 = 7.5 Hz, J_2 = 5.5 Hz); 7.19 (t, 1 H, J = 8.4 Hz); 7.45—7.62 (m, 4 H); 7.76 (d, 1 H, J = 6.5 Hz); 7.86 (t, 2 H, J = 9.4 Hz); 8.44 (d, 1 H, J = 8.3 Hz). ^{13}C NMR (100 MHz, DMSO-d$_6$), δ: 114 (C(1)); 115.32 (C(2)); 116.13 (C(3)); 121.51 (C(4)); 123.54 (C(5)); 127.26 (C(6)); 128.08 (C(7), C(8)); 130.94 (C(9)); 131.61 (C(10), C(11)); 134.54 (C(12)); 138.47 (C(13)); 157.71 (C(14)); 163.10 (C(15)).

The structures of the obtained products were confirmed by ^{1}H and ^{13}C spectroscopy.

^{1}H and ^{13}C NMR spectra were measured on a Bruker AM300 spectrometer (solvents $CDCl_3$ and DMSO-d$_6$), and the data of HSQC, HMBC, APT, and NOESY procedures were used for signal assignment.



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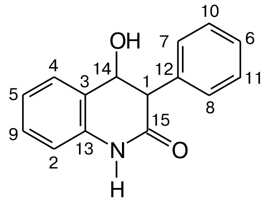

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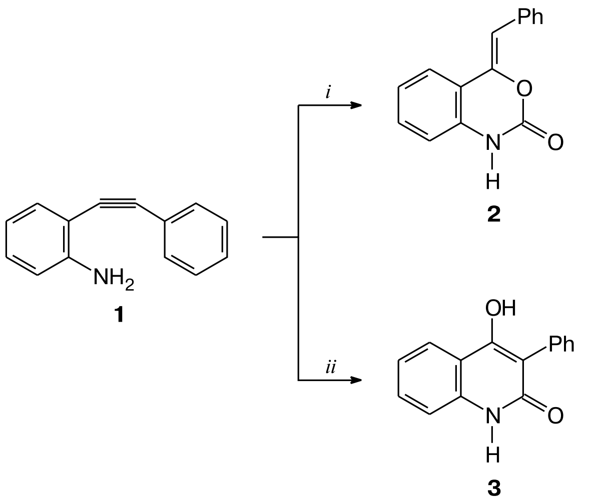
Diffuse reflectance infrared Fourier transform spectra (DRIFTS) were recorded at ~20 °C on a Nicolet 460 Protégé spectrometer with the diffuse reflectance attachment. Catalyst samples were placed in ampules with a KBr window, and a CaF_2 powder served as a reference sample. For a satisfactory signal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

The phase composition of catalyst samples was determined by X-ray diffraction analysis. The XRD patterns were collected on a Dron-3 instrument using Cu-Kα radiation (λ = 0.1542 nm). The samples were scanned in the 2θ range of 5—60° at 1° min of scan speed. The size of coherent scattering region (D_{CSR}, Å) was determined taking the peak width at half heights for the signal at 38.1 Å corresponding to the metallic silver phase. The diffractograms were compared with the JCPDS-ICDD and ICDS references.

Results and Discussion

According to the literature data,[8—10] the catalytic transformations of 2-(2-phenylethynyl)aniline under the action of Ag^+ salts can proceed *via* two routes (Scheme 1) with the direction depending on the reaction conditions (CO_2 pressure, nature of the used base).

Scheme 1



i. Ag^+, CO_2 (10 atm), DABCO, DMSO, ~20 °C; *ii.* Ag^+, CO_2 (1 atm), DBU, DMSO, 60 °C.

The both reactions were carried out in the presence of silver nitrate and bases DABCO or DBU in a DMSO medium (Table 2, entry *1* and Table 3, entry *1*). The isolated yields of compounds **2** and **3** were 80 and 83%, respectively.

It was established that the reactions in the absence of bases afforded the products in stoichiometric amounts only (see Table 2, entry *5* and Table 3, entry *3*). No formation of the products was observed in the absence of silver salts in the mixture (see Table 2, entries *2* and *3*; Table 3, entry *2*).

The catalytic reactions in which the triple bond of the substrate is activated by silver ions are often carried out in the presence of inorganic base, cesium carbonate.[6,7,11] The obtained results show that in the studied reactions the replacement of organic bases DABCO and DBU by Cs_2CO_3 lead only to an insignificant decrease in the yield of the target products (see Table 2, entry *4*; Table 3, entry *4*).

It was also established that the replacement of silver nitrate by copper iodide does not result in the formation of target product **2** (see Table 2, entry *6*).

The choice of the heterogeneous Ag-containing catalysts for the synthesis of compounds **2** and **3** was made on the basis of our earlier results.[11] The study of the direct carboxylation of phenylacetylene by carbon dioxide showed that the isolated yields of the targeted phenylpropionic acid exceeding 50% are achieved on the heterogeneous Ag-containing catalysts Ag(5%)/TiO_2, Ag(20%)/SiO_2, and Ag(0.5%)/γ-Al_2O_3(F). The testing of these three catalysts in the reaction of formation of benzoxazin-2-one **2** showed that the targeted product was formed only on the Ag(1%)/Al_2O_3(F) catalyst (see Table 3).

We assumed that the activity of the Ag(1%)/Al_2O_3(F) catalyst in the reactions proceeding through the activation of the triple bond of the substrate is explained by the presence of acid sites on the support surface. The sites are formed upon the modification of alumina by fluorine anions. Therefore, we synthesized the Ag-containing catalysts on fairly acidic supports (W—ZrO_2, zeolite H-Beta). The use of these catalysts in the reactions producing prod-

Table 2. Yields of benzoxazin-2-one **2** on the Ag-containing catalysts[a]

Entry	Catalyst	Base	τ/h	Isolated yield of target product (%)
1	$AgNO_3$	DABCO	24	80
2	—	DABCO	44	—
3	—	Cs_2CO_3	28	—
4	$AgNO_3$	Cs_2CO_3	24	70
5	$AgNO_3$	—	24	8
6	CuI	DABCO	45.5	—
7	Ag(1%)/W—ZrO_2	DABCO	76.5	Traces
8	Ag(20%)/SiO_2	DABCO	57	—
9	Ag(5%)/TiO_2	DABCO	37.5	—
10	Ag(2%)/APTES—MCM-41	DABCO	42.5	—
11	Ag(1%)/Al_2O_3(F)	DABCO	50	40
12[b]	Ag(1%)/Al_2O_3(F)	DABCO	35	—
13[c]	Ag(1%)/Al_2O_3(F)	DABCO	44.5	—
14	Ag(1%)/Al_2O_3(F)	Cs_2CO_3	46	60

[a] Reaction conditions: ~20 °C, $P(CO_2) = 10$ atm, 0.125 mmole of substrate, 0.0125 mmole of Ag, 0.025 mmole of base, DMSO as solvent (1 mL).

[b] $P(CO_2) = 20$ atm.

[c] $T = 50$ °C.

Table 3. Yields of 4-hydroxyquinolin-2(1*H*)-one **3** on the Ag-containing catalysts*

Entry	Catalyst	Base	τ/h	Isolated yield of target product (%)
1	$AgNO_3$	DBU	24	83
2	—	DBU	35.5	—
3	$AgNO_3$	—	45.5	7
4	$AgNO_3$	Cs_2CO_3	40.0	75
5	Ag(1%)/H-Beta	DBU	50	—
6	Ag(2%)/APTES—MCM-41	DBU	32.5	8
7	$Ag(1\%)/Al_2O_3(F)$	DBU	37.5	10
8	$Ag(1\%)/Al_2O_3(F)$	Cs_2CO_3	38.5	30

* Reaction conditions: $T = 60$ °C, $P(CO_2) = 1$ atm, 0.3 mmole of substrate, 0.03 mmole of Ag, 0.3 mmole of base, DMSO as solvent (2—3 mL).

ucts **2** and **3** showed that benzoxazin-2-one **2** was formed on the Ag(1%)/W—ZrO_2 catalyst in trace amounts (see Table 2, entry *7*), and the Ag(1%)/H-Beta catalyst is inactive in the formation of 4-hydroxyquinolin-2(1*H*)-one **3** (see Table 3, entry *5*).

The heterogeneous catalysts Ag(1%)/γ-Al_2O_3(F), Ag(1%)/Beta, and Ag(1%)/W—ZrO_2 were studied by DRIFTS spectroscopy. The IR spectra in the region of OH groups detected on these catalysts are presented in Fig. 1.

The bands of OH groups of three types are observed in the spectrum of the Ag(1%)/Al_2O_3(F) sample treated *in vacuo* at 450 °C for 1 h. The band at 3709 cm^{-1} characterizes stretching vibrations of hydroxyls that function as strong Brönsted acid sites. The formation of these sites is associated with the partial substitution of the basic hydroxyl groups of the =Al—O—H fragments by fluorine.[12—14] The band at 3663 cm^{-1} is assigned to stretching vibrations of the bridging OH groups, whereas the broad band with the center at ~3569 cm^{-1} can be ascribed to stretching vibrations of the hydrogen-bonded hydroxyl groups that act as acid sites.

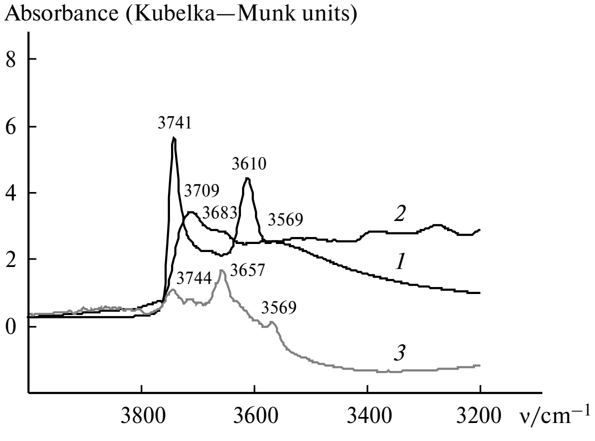


Fig. 1. DRIFT spectra in the range of stretching vibrations of OH groups in the catalysts Ag(1%)/Al_2O_3(F) (*1*), Ag(1%)/H-Beta (*2*), and Ag(1%)/W—ZrO_2 (*3*).

Two bands are observed in the spectrum of compound Ag(1%)/Beta. The band at 3741 cm^{-1} belongs to stretching vibrations of isolated ≡Si—O—H groups, whereas the band at 3610 cm^{-1} characterizes strong bridged Brönsted acid sites.

The spectrum of the sample Ag(1%)/W—ZrO_2 contains three low-intensity bands. The band at 3744 cm^{-1} is attributed to stretching vibrations of isolated ≡Zr—O—H groups, the band at 3657 cm^{-1} corresponds to the bridging OH groups bonded to several zirconium ions, and the band at 3569 cm^{-1} is characteristic of the hydrogen-bonded acid sites.

Experiments on the adsorption of a testing molecule of carbon monoxide were carried out to determine the charge state of silver in the catalysts. Adsorption of CO on all the three samples does not result in any changes in the region of the spectra that contains vibrations of OH groups.

The spectra recorded during CO adsorption—desorption on the Ag(1%)/F—Al_2O_3, Ag(1%)/Beta, and Ag(1%)/W—ZrO_2 catalysts are presented in Figs. 2, 2, *a*, *b*, and *c*.

Two bands at 2215 and 2190 cm^{-1} appear in the spectrum of the Ag(1%)/Al_2O_3(F) after CO adsorption. The first band disappears completely upon short-term evacuation at ~20 °C.

It is known[12,15] that CO is not adsorbed at ~20 °C on Ag^0 and carbonyls on metallic silver are detected in a vicinity of 2060 cm^{-1} only at low temperatures[16] or at 2099 cm^{-1} at high equilibrium pressures.[17] Therefore, the band at 2190 cm^{-1} can be assigned to stretching vibrations of CO molecules adsorbed on the Ag^+ cations,[12,15] and the band at 2215 cm^{-1} can be attributed to vibrations of CO molecules adsorbed on the coordinatively unsaturated Al^{3+} ions.[12,15]

The spectrum of the Ag(1%)/Beta catalyst (see Fig. 2, *b*) exhibits a band at 2184 cm^{-1}, whereas the spectrum of the Ag(1%)/W—ZrO_2 catalyst (see Fig. 2, *c*) contains a band at 2192 cm^{-1}. The both bands belong to stretching vibrations of CO molecules adsorbed on Ag^+ cations.

It is known that size effects are more characteristic of the Au-containing catalysts than for the Ag-containing

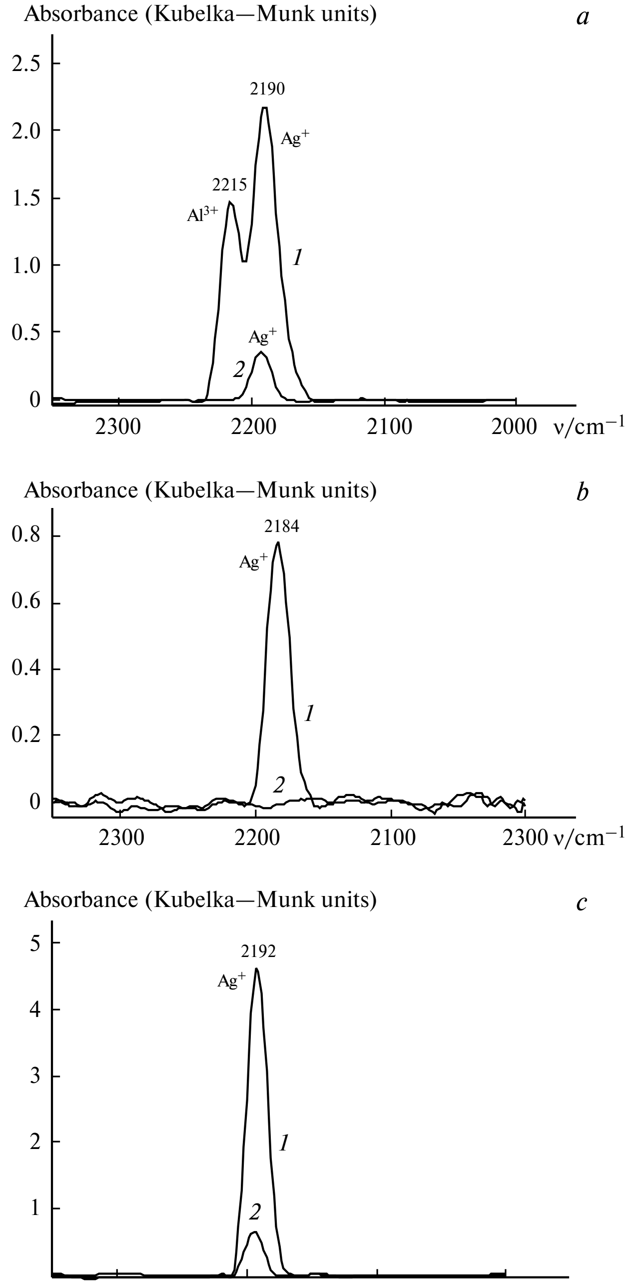


Fig. 2. DRIFT spectra of the reduced catalysts after CO adsorption at 20 °C and a pressure of 10 Torr (*1*) and after evacuation at 20 °C for 1 min (*2*): Ag(1%)/Al_2O_3 (*a*), Ag(1%)/H-Beta (*b*), and Ag(1%)/W—ZrO_2 (*c*).

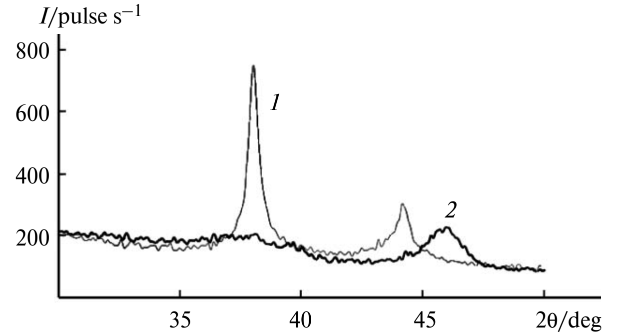


Fig. 3. X-ray patterns of the samples Ag(1%)/SiO_2 (particle size of metallic silver 15 nm) (*1*) and Ag(1%)/Al_2O_3(F) (size of Ag particles <2 nm) (*2*).

catalysts. However, the X-ray phase analysis of the catalysts (Table 4) showed that only the samples with the silver particle size <2 nm (Ag(1%)/Al_2O_3(F) and Ag(1%)/W—ZrO_2) were active in the studied reactions.

The X-ray patterns of two catalyst samples are presented in Fig. 3: Ag(1%)/SiO_2 in which the particle size of metallic silver is 15 nm, according to the X-ray phase analysis data, and the Ag(1%)/(Al_2O_3(F) sample with the metal particle with the size <2 nm.

Taking into account the foregoing results, we synthesized the catalyst Ag(1%)/APTES—MCM-41 in which the surface of the initial mesoporous silicate was pre-modified by amino groups to provide high dispersion of silver. This made it possible to obtain metal particles with the size <2 nm (see Table 4, entry *5*). However, this catalyst was inactive in the reactions of interest (see Tables 2 and 3).

Thus, it is established that only the Ag(1%)/γ-Al_2O_3(F) samples has a noticeable catalytic activity in the reactions of synthesis of benzoxazin-2-one **2** and 4-hydroxyquinolin-2(1*H*)-one **3** (see Tables 2 and 3).

An increase in temperature and in CO_2 pressure to 20 atm during the synthesis of benzoxazin-2-one **2** does not increase the yield of the target product (see Table 3). The better yields of both products are achieved when cesium carbonate is used as a base (see Tables 3 and 4).

To conclude, we succeeded to develop the heterogeneous catalysts for the both reactions. The best result was achieved with the Ag(1%)/Al_2O_3(F) catalyst. For the synthesis of benzoxazin-2-one **2**, the maximum yield of the targeted product on this catalyst was 40 or ~60% when

Table 4. Size of silver particles and sorption capacity of the heterogeneous Ag-containing catalysts

Entry	Catalyst	Size of Ag^0 particles/nm	State of adsorbed CO
1	Ag(1%)/Al_2O_3(F)	<2	Complex CO—Ag^+
2	Ag(20%)/SiO_2	15	Was not studied
3	Ag(1%)/W—ZrO_2	<2	Complex CO—Ag^+
4	Ag(5%)/TiO_2	27	Was not studied
5	Ag(2%)/APTES—MCM-41	<2	No sorption
6	Ag(1%)/H-Beta	25	Complex CO—Ag^+

the standard base DABCO or sodium carbonate, respectively, were used. The maximum yield of the target product in the synthesis of 4-hydroxyquinolin-2(1*H*)-one **3** was 10 and ~30% in the presence of the standard base DBU and cesium carbonate, respectively.

The results of physicochemical studies indicate that the high activity of the catalysts in the reactions proceeding *via* triple bond activation is explained by a combination of three factors. First, the catalyst contains nanoparticles of metallic silver <2 nm in size. Second, metallic silver particles coexist with silver cations. Third, strong acid sites are present in the support surface.

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