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Cu and Au nanocomposites in catalytic olefination reaction

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Metal-vapor synthesis-prepared Cu, Ag, Au and bimetallic Au–Cu (optimal) nanocomposites catalyse olefination of hydrazones with polyhalomethanes.

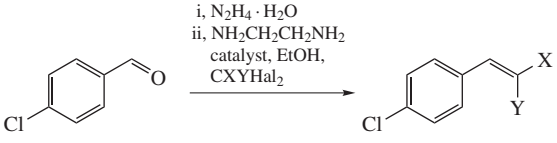
Transformation of carbonyl compounds to olefins is one of the most common approaches to the construction of new C=C bonds.[1] A new catalytic olefination reaction (COR), developed in our group, consists in interaction of hydrazones of carbonyl compounds with polyhaloalkanes in the presence of copper salts (0.1–10 mol%). High applicability of COR gave rise to a great variety of alkenes starting from available and cheap reagents by a simple experimental technique.[2] An attractive challenge for further development of COR is the use of heterogeneous catalysts, which is advantageous of easy separation from reaction products and multiple re-use of catalytic material. All of that makes the reaction environmentally more friendly.

High activity of Cu, Cu–Au and Cu–Ag heterogeneous systems have been demonstrated previously.[3] Hence, one can expect that mono- and bimetallic copper-containing heterogeneous catalysts can be also good in COR. In addition, it is very interesting to study the influence of another valence state of copper on the reaction outcome. Such states are realized in the particles of Au–Cu bimetallic nanosystems deposited on Al_2O_3 and SiO_2 supports by metal-vapor synthesis (MVS). Mono- and bimetallic nanoparticles prepared by MVS demonstrated effective magnetic,[4] antibacterial[5] and catalytic properties.[6] Moreover, nanoparticles of Au and Cu obtained by MVS are intensively studied in various catalytic processes.[7] Here, we would like to present the synthesis and study of the catalytic activity of MVS obtained mono- and bimetallic Cu and Au–Cu/X (X = Al_2O_3, SiO_2) systems in COR.†

Since hydrazones are the true reactants in COR, it should be expected that this process will be very sensitive to the catalyst due to the active copper leaching by complexation with hydrazine derivatives. Thus, we have observed in preliminary experiments that heterogeneous catalysts, based on copper complexed with immobilized amine, become completely inactive after the first cycle of reaction.

We tested eight mono- Au, Ag, Cu and bimetallic Au–Cu nanosystems deposited on Al_2O_3 and SiO_2 (Scheme 1, Table 1). Hydrazone of 4-chlorobenzaldehyde, CCl_3Br and CCl_4 were chosen for model reactions to search for optimal catalyst. Reaction was carried out during 24 h in ethanol using ethylenediamine as a base. Cu and Au catalysts **6**, **7** and **8** provided the best results. The yields of alkene for CCl_4 and CCl_3Br were comparable with those obtained using homogeneous catalysis. In contrast, Ag- and Au-containing catalysts **1**, **3** and **4** appeared to be considerably less effective. Obtained by the modification of monometallic copper system **2**, bimetallic Cu–Au system **7** demonstrates the synergetic effect giving higher yields. We also found that the manner of catalyst synthesis is not crucial for its activity. Thus, successive deposition of metals in the case of **5** gave yields of alkenes compared to those for simultaneous deposition used in **6**. Other polyhaloalkanes were also involved into the reaction using most active catalysts **6**, **7** and **8** (Table 2). A series of experiments with varying of the amount of catalyst clarified that it is optimal to use 150 mg of catalyst **6**, **7** or **8** for 5 mmol of hydrazone.

Three catalytic cycles were carried out for each polyhalomethane with separation and re-use of the catalyst (Table 2). In case of the most active $CHBr_3$, CCl_3Br and CBr_3F repeated reactions were possible, but with noticeable decrease in the reaction yield. Nevertheless, non-zero yields were detected even after the third reaction cycle. This fact clearly indicated, that heterogeneous catalysts provided results comparable with those for



CCl_4, X = Y = Cl
$CBrCl_3$, X = Y = Cl
$CFBr_3$, X = F, Y = Br
$CHBr_3$, X = H, Y = Br

Scheme 1

Table 1 Catalyst for catalytic olefination reaction: active metal components and content.

Catalyst	Metal/ Support	Content of metal (%)	Mmol of active metal (%)	Yield of alkene (%)	
				from CCl_3Br	from CCl_4
1	Au/Al_2O_3	0.09	0.015	41	2
2	Cu/Al_2O_3	0.23	0.12	58	45
3	Ag/SiO_2	0.16	0.047	65	4
4	Ag/Al_2O_3	0.45	0.133	67	6
5	Cu–Au/ Al_2O_3	Cu, 0.033 Au, 0.015	Cu, 0.016 Au, 0.0024	75	42
6	Cu, Au/ Al_2O_3	Cu, 0.096 Au, 0.023	Cu, 0.048 Au, 0.0037	73	59
7	Cu, Au/ Al_2O_3	Cu, 0.023 Au, 0.02	Cu, 0.012 Au, 0.0032	81	65
8	Cu/SiO_2	0.46	0.23	81	70

Table 2 The yields of alkenes depending on catalyst (%).[a]

Polyhalomethane	6			7			8		
	I	II	III	I	II	III	I	II	III
CCl_3Br	73	46	35	81	62	40	81	39	35
CCl_4	59	8	5	65	33	16	70	23	8
CBr_3F	73	11	8	71	52	17	70	24	10
$CHBr_3$	66	9	3	63	29	11	64	25	11

[a]The reaction is accompanied by the formation of the corresponding azine as a major by-product.

homogeneous catalysts. The decline of catalytic activity is probably due to leaching of copper nanoparticles from catalysts as well as simple mechanical destruction of catalyst granules in the course of the reaction. It should be noted that bimetallic Cu–Au system **7** showed higher yields for the second and third cycles comparing to those for monometallic Cu system **8**. One can attribute that to the stabilizing effect of Au, which prevents leaching of Cu from the catalyst. Additional explanation can be regarded to the synergism between Cu and Au.

Au–Cu nanocomposites were studied by X-ray photoelectron spectroscopy as well as transmission electron microscopy (TEM) to have insight into catalyst structure and size distribution. Quantitative analysis using relative sensitivity factors developed for Kratos XSAM-800 gave composition $C_{0.28}O_{0.25}Cu_{0.13}Al_{0.34}Au_{0.001}$ for the Au–Cu/Al_2O_3 system. Intensity ratio of the main and satellite peaks in the spectrum of Cu 2*p* indicates that the spectrum contains at least two states of copper atoms, Cu^{2+} and Cu^+ or Cu^0. The Cu $2p_{3/2}$ peak occupied an intermediate position between those of Cu^{2+} and Cu^+ and/or Cu^0 states (Figure 1).

The Cu 2*p* photoelectron spectra of the Au–Cu/Al_2O_3 nanocomposite are practically independent of bias voltage applied to the sample holder. In contrast, positive biasing the sample (Figure 1) leads to noticeable broadening of the Au 4*f* and total Al 2*p* + Cu 3*p* peaks. Analysis of the Cu 3*p* peak is difficult owing to superposition of the Al 2*p* and Cu 3*p* peaks. Binding energy position of the Au $4f_{7/2}$ peak at 84.3 eV indicates a metallic state of gold and a manifestation of the size effect. The O 1*s* spectrum is also depends on the bias voltage. The dependence

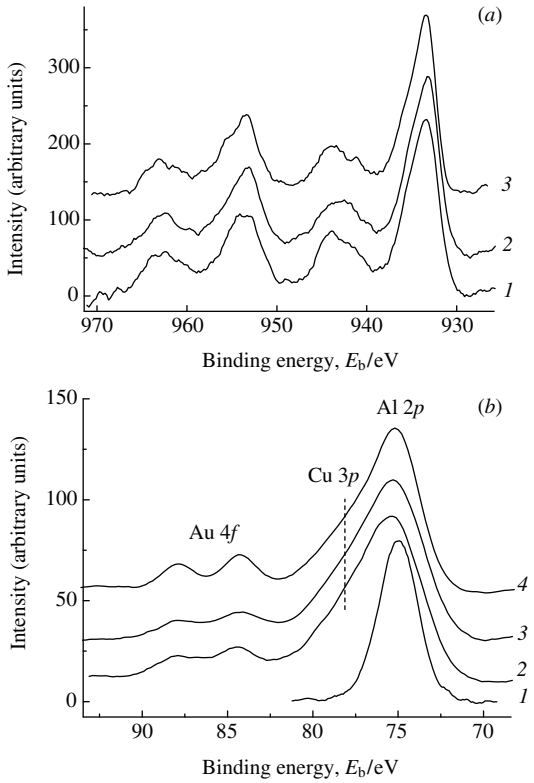


Figure 1 (*a*) Cu 2*p* photoelectron spectra of Au–Cu/Al_2O_3 nanocomposite measured at U_b: (*1*) 0, (*2*) –7 and (*3*) +7 V. (*b*) Photoelectron spectra of (*1*) Al_2O_3 support and Au–Cu/Al_2O_3 nanocomposite measured at U_b: (*2*) 0, (*3*) –7 and (*4*) +7 V.

reflects the heterogeneity of the sample and the presence of copper in the oxidized state. The difference in the O 1*s* spectra of the support and the nanocomposite in the low energy region is also associated with the presence of oxidized copper.

Typical TEM micrograph of the Cu/SiO_2 nanocomposites is presented in Figure 2. For sample **8**, some differences in the average size of stabilized metal particles, measured before and after the catalytic tests were observed. The initial sample consists of particles with an average size of 12.2 nm, which is about twice higher than that measured after olefination (6.2 nm). This result can be explained considering that TEM image of the original sample shows that copper nanoparticles contain small fragments with sizes of 4.7 nm, which are grouped into clusters and can be washed out from the support during the catalytic experiments. For system **1**, gold particles with an average size of 3.6 nm and aggregates 6.5–8.6 nm consisting of smaller entities were observed. As can be seen in the photos the chain length of particles is 30–84 nm and a transverse size is 2.5–3.0 nm.

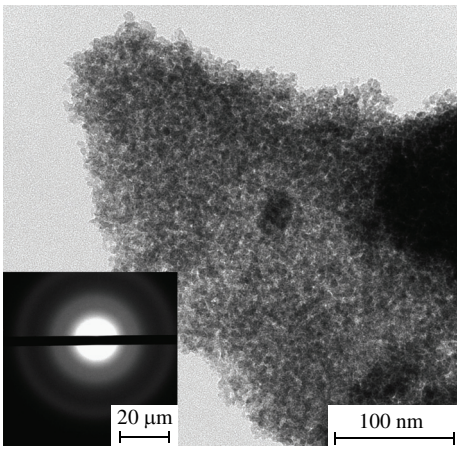


Figure 2 TEM photograph of **8**. Inset: image of electronogram.

† Catalysts were obtained by the MVS method for the preparation of mono- and bimetallic systems using earlier reported technique.[4] Copper (shavings, 99%), gold (foil, 99.99%), toluene (99%, Aldrich), triethylamine (99%, Aldrich), SiO_2 (Kieselgel, 70–270 mesh, 60 Å, Aldrich), γ-Al_2O_3 (IKT-02-6 M from JSC 'Katalizator', Novosibirsk, S = 138 m^2 g^{-1}) have been used. In typical experiments, 0.1–0.3 g of metal were evaporated from tantalum boats with 100–150 ml of solvent; 3–5 cm^3 of the supports were modified by the obtained metal organosols in a vacuum. The supports were previously activated by calcinations at 300 °C in a vacuum. The XPS measurements were performed at room temperature on an XSAM-800 spectrometer (Kratos Analytical, UK) with non-monochromatic MgKα radiation. Data were acquired at 15 kV and 6 mA under the vacuum of ~5×10^{-8} Pa. Spectra were recorded in the fixed retarding ratio mode. Photoelectron spectra were recorded with a step of 0.1 eV. After subtraction of a linear background, a Gaussian function was used to deconvolve the measured spectra. The energy scale of the spectrometer was calibrated against the following peaks: the Au $4f_{7/2}$ (84.0 eV), the Ag $3d_{5/2}$ (368.3 eV) and the Cu $2p_{3/2}$ (932.7 eV). The atomic concentration has been determined from C 1*s*, O 1*s*, Al 2*p*, Cu 2*p* and Au 4*f* XPS peak areas using linear background subtraction and atomic sensitivity factors provided by the spectrometer manufacturer. The samples were secured to a titanium holder in air using two-sided conductive adhesive tape. To compensate for X-ray induced surface charging all the binding energies were referred to the C–C,H peak at 285.0 eV in the fitted C 1*s* spectrum (support) and to the Al 2*p* (75.0 eV) (nanocomposite). Micrographs were obtained using a LEO 912 AB OMEGA, Zeiss (Germany) microscope. COR with heterogeneous catalysts was carried out using previously reported standard procedure for the homogeneous ones.[2] ^{1}H NMR data of alkenes were identical to literature data.[2]

In summary, the use of heterogeneous catalysts in the catalytic olefination reaction gave comparable to homogeneous catalysis results. Synergetic effect of bimetallic catalysts in Cu–Au nanoparticles in comparison with monometallic particles of copper was found. The promising direction of further investigations is a search of heterogeneous catalysts resistant to leaching.

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