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Synergism of the Catalytic Effect of Nanosized Gold–Nickel Catalysts in the Reaction of Selective Acetylene Hydrogenation to Ethylene

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Abstract—Gold and nickel nanoclusters immobilized on aluminum oxide exhibited high activity in the reaction of acetylene hydrogenation to ethylene with molecular hydrogen at temperatures from 20 to 64°C. The reaction selectivity on Au–Ni nanocomposites with metal concentrations from 0.02 to 0.36 wt % was no lower than 99.99%, and the stability of catalysts was retained for at least 12 h. The simultaneous presence of gold and nickel in the systems resulted in the synergism of their catalytic effects: acetylene conversion on layer-by-layer immobilized metal clusters was higher than the total conversion on individual gold and nickel clusters. The dependence of the conversion of acetylene on bimetallic catalysts on the Au : Ni ratio exhibited an extremal character.

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INTRODUCTION

The total concentration of acetylene derivatives and polyenes in commercial ethylene is about 1–3%, and acetylene accounts for to 80% of this value [1, 2]. However, even these trace impurities of C_2H_2 are responsible for the rapid poisoning of metal complex catalysts for ethylene polymerization, and they dramatically impair the quality of the resulting polymers. The maximum permissible concentration of acetylene in the raw monomer should be no higher than 10 ppm [3, 4]. This problem is currently solved by the selective hydrogenation of acetylene derivatives. This process occurs most efficiently in the presence of bimetallic catalysts based on ultradispersed Pd and Ag particles with weight concentrations of the supported metals from 0.02 to 0.3% [5, 6]. However, in spite of high selectivity, these catalysts are not ideal, because they are rapidly poisoned by oligomer by-products. Thus, the development of new high-performance and efficient catalysts for selective hydrogenation is a problem of considerable current interest. In this respect, catalytic systems based on gold and nickel nanoclusters, which exhibit a strong synergistic catalytic effect allyl isomerization (this reaction occurs by a mechanism similar to the mechanism of hydrogenation), seem promising. The synergistic effect manifests itself in an increase in the catalytic activity of the bimetallic system by three or more orders of magnitude, as compared with the total activity of individual gold and nickel [7–11].

In this paper, we report the results of a study of the selective hydrogenation of acetylene to ethylene in the presence of bimetallic composites based on layer-by-layer immobilized gold and nickel clusters.

EXPERIMENTAL

Starting Materials

High-purity ethylene, acetylene, and hydrogen were used as reactants. Microspherical γ-Al_2O_3 of the IKT-02-6M brand from AO Katalizator with the specific surface area $S_{sp} = 138$ m^2/g and the total pore volume of 0.32 cm^3/g served as a support for nanoparticles. Before use, γ-Al_2O_3 was activated by calcination at 350°C for 3 h. To prepare the catalysts, $HAuCl_4 \cdot nH_2O$ (Aurate, TU [Technical Specifications] 6-09-05-1075-89) with an Au content of 49.04 wt %, $Ni(NO_3)_2 \cdot 6H_2O$ (Reakhim, analytical grade), $PdCl_2 \cdot nH_2O$ (Aldrich, no. 205885) with a $PdCl_2$ content of 99 wt %, distilled water, and a 0.1 M aqueous solution of NaOH were used.

Catalyst Preparation

Gold nanoparticles supported on γ-Al_2O_3 were formed using a previously published anion adsorption procedure [9]. In the preparation of an Au/γ-Al_2O_3 catalyst, the value of pH 7 in an aqueous solution of $HAuCl_4$ was usually adjusted by the addition of sodium hydroxide. A calculated amount of the calcined support was introduced into the neutralized pre-

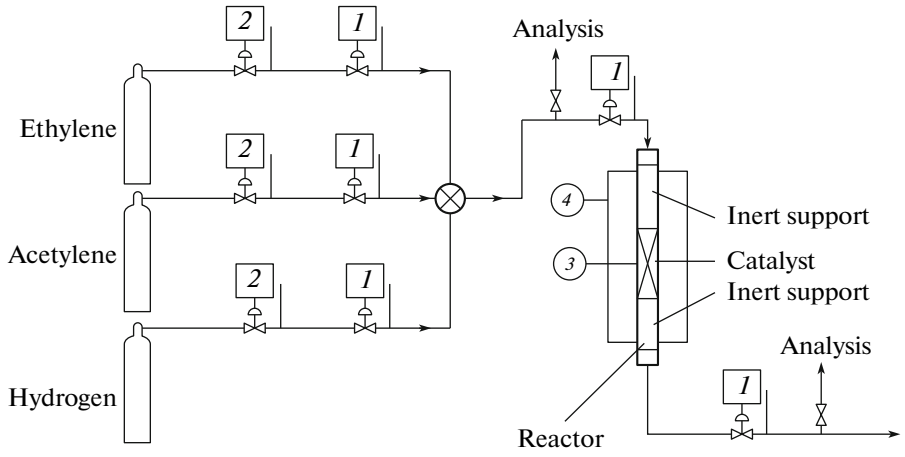

Fig. 1. Schematic diagram of the system for acetylene hydrogenation in the presence of ethylene: (*1*) pressure indicator, (*2*) gas flow regulator, (*3*) thermocouple, and (*4*) temperature regulator.

cursor solution, and the resulting suspension was stirred at 70°C for 1 h. The catalyst precursor was separated from mother liquor, washed with distilled water, dried in air for a day, and calcined at 300°C in an inert atmosphere for 3 h. In this manner, the Au/γ-Al_2O_3 catalysts with metal concentrations from 0.02 to 0.27 wt % were prepared.

Nickel nanoparticles supported on γ-Al_2O_3 were formed by incipient wetness impregnation [10]. To prepare a Ni/γ-Al_2O_3 catalyst, a calculated amount of an aqueous solution of nickel nitrate was added to the support calcined at 350°C; the contents were dried in air for a day, calcined at 300°C in an inert atmosphere for 3 h, and reduced in a flow of hydrogen. In this manner, the Ni/γ-Al_2O_3 catalyst with a metal concentration of 0.09 wt % was prepared.

The Au–Ni/γ-Al_2O_3 bimetallic catalysts were formed layer by layer: initially, an Au/γ-Al_2O_3 catalyst was prepared by the anion adsorption of dissolved $HAuCl_4$ on γ-Al_2O_3; then, the second metal was supported by the impregnation of calcined Au/γ-Al_2O_3 with an aqueous solution of nickel nitrate. In this manner, the Au–Ni/γ-Al_2O_3 catalysts with gold and nickel concentrations of 0.02–0.27 and 0.002–0.09 wt %, respectively, were prepared.

The Pd–Ag/γ-Al_2O_3 bimetallic catalyst was formed in a similar way: initially, a Pd/γ-Al_2O_3 catalyst was prepared by the anion adsorption of $PdCl_2$; then, the second metal was supported by impregnation with an aqueous solution of silver nitrate. The resulting Pd–Ag/γ-Al_2O_3 catalyst contained 0.02 wt % of palladium and 0.02 wt % silver.

Determination of the Weight Concentrations of Metals

A metal (or metals) supported on the catalyst surface was washed from the support with a solution of a mixture of concentrated acids (HCl : HNO_3 = 3 : 1). The weight concentrations of the metals in solution were found by atomic absorption spectrometry on a Hitachi 180-80 spectrometer. The relative error in the determination of metal concentrations over the range of 5×10^{-6}–5×10^{-5} g/l was no higher than 1%.

Gas-Phase Acetylene Hydrogenation in Flowing Ethylene

A mixture of ethylene and acetylene was hydrogenated in a flow system with a Pyrex glass reactor (Fig. 1). The following standard reaction conditions were used: hydrogen, acetylene, and ethylene flow rates of 1, 0.5, and 10 ml/min, respectively, and a catalyst sample weight of 1 g. The reaction temperature was varied over a range from 20 to 64°C. The reaction products were sampled at the outlet of the flow system and analyzed by GLC on a Chrom-800 chromatograph (a 3-m column with Poropak T; temperature, 50°C; carrier gas, He; and detector, FID).

The conversion of acetylene $x_{C_2H_2}$ was calculated by the equation

$$x_{C_2H_2} = ([C_2H_2]_0 - [C_2H_2]_t)[C_2H_2]_0^{-1} \times 100\%,$$

where $[C_2H_2]_0$ is the mole fraction of acetylene in the organic mixture before reaction, and $[C_2H_2]_t$ is the mole fraction of acetylene in the organic mixture after the onset of reaction at point t in time.

The selectivity was found from the equation

$$S = [C_2H_4]_t([C_2H_2]_t + [C_2H_4]_t + [C_2H_6]_t)^{-1} \times 100\%,$$

where $[C_2H_2]_t$, $[C_2H_4]_t$, and $[C_2H_6]_t$ are the mole fractions of acetylene, ethylene, and ethane, respectively, in the organic mixture after the onset of reaction at point t in time.

RESULTS AND DISCUSSION

The table summarizes data on the conversion of acetylene into ethylene and the selectivity of the reactions that occur on the support, on the monometallic

Hydrogenation of a mixture of ethylene and acetylene on the $Au/\gamma\text{-}Al_2O_3$, $Ni/\gamma\text{-}Al_2O_3$, and $Au–Ni/\gamma\text{-}Al_2O_3$ catalysts and the $\gamma\text{-}Al_2O_3$ support under standard conditions

Catalyst	Metal content of the catalyst, wt %		Reaction temperature, °C	Reaction time, min	$x_{C_2H_2}$, %
	Au	Ni			
$\gamma\text{-}Al_2O_3$	–	–	20	5	5
			20	30	7
			20	55	2
			20	116	4
$Au/\gamma\text{-}Al_2O_3$	0.27	–	20	20	3
			20	34	4
			20	67–160	3
$Ni/\gamma\text{-}Al_2O_3$	–	0.09	20	15	4
			20	34	7
			20	67–200	13–14
$Au\text{-}Ni/\gamma\text{-}Al_2O_3$	0.27	0.09	20	15	79
			20	30–720	83
$Au\text{-}Ni/\gamma\text{-}Al_2O_3$	0.02	0.006	20	15–250	69
			59	5	84
			59	30	84
			59	60	80
			64	120	86
$Au\text{-}Ni/\gamma\text{-}Al_2O_3$	0.02	0.002	20	15	32
			20	30	31
			20	45–200	34
			36	20	39
			40	40	48
			38	60	42
			54	60	54
			58	80	62
			61	98	61
			62	117	59
			64	154	71
$Au\text{-}Ni/\gamma\text{-}Al_2O_3$	0.02	0.02	20	15–260	36–38
			55	60	64
			56	75	69
			55	90	65
			58	280	64

catalysts based on gold and nickel, and on mixed gold–nickel systems. As can be seen, hydrogenation occurred on the support ($\gamma\text{-}Al_2O_3$) with a low yield of about 2–7%. As follows from published data [2], the catalytic effect of pure $\gamma\text{-}Al_2O_3$ at 20°C seems unlikely. It is most likely that the above experimental result can be explained by the presence of iron and other metal trace impurities in aluminum oxide.

The table also indicates that the conversion of acetylene on immobilized monometallic gold clusters at 20°C was comparable with the conversion on the support. This is consistent with published data [12], according to which gold exhibited noticeable activity in the hydrogenation reaction at temperatures higher than 125°C, when the dissociative adsorption of hydrogen occurred on the surface of nanoclusters [13]. The conversion of acetylene on nickel at 20°C was also low, and it did not exceed 14%.

The introduction of nickel nanoparticles along with gold at the stage of formation dramatically increased the conversion of acetylene. The conversion of acetylene on an Au–Ni catalyst was much higher

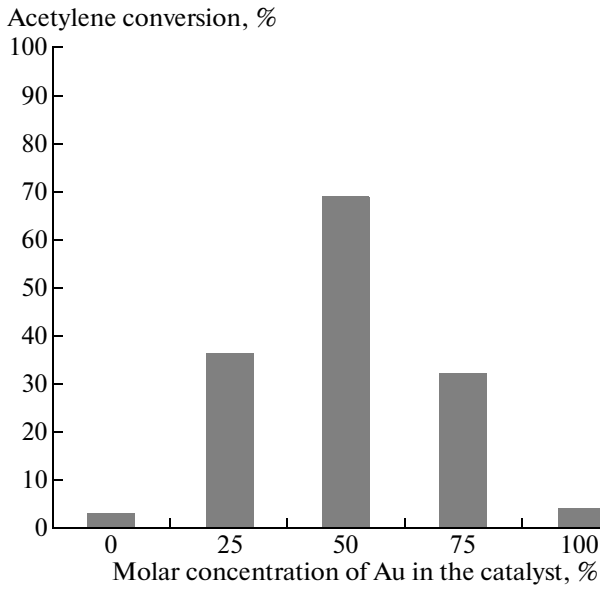

Fig. 2. Dependence of acetylene conversion on the molar concentration of gold in the Au–Ni/γ-Al_2O_3 catalyst. Reaction conditions: temperature, 20°C; C_2H_4, C_2H_2, and H_2 flow rates, 10, 0.5, and 1 ml/min, respectively; [Au] + [Ni] = 0.02–0.04 wt %; catalyst sample weight, 1 g; and reaction time, 15–20 min.

than the sum of conversions on individual metals, all other factors being the same. Thus, the conversion of acetylene into ethylene on the Au–Ni/γ-Al_2O_3 catalyst ([Au] = 0.27 wt %, [Ni] = 0.09 wt %) 30 min after the onset of passing the reaction mixture was 83%, whereas the overall conversion on Au/γ-Al_2O_3 ([Au] = 0.27 wt %) and Ni/γ-Al_2O_3 ([Ni] = 0.09 wt %) was only 16–17%. In this case, the time of the stable operation of a gold–nickel catalyst was no shorter than 12 h. The reaction selectivity on all of the catalysts over the entire test temperature range was ≥99.99%.

A decrease in the total metal concentration by approximately an order of magnitude with the retention of approximately the same Au : Ni ratio did not exert considerable influence on the selectivity and stability of the bimetallic catalyst, and it was accompanied by only a decrease in the conversion of acetylene (cf. data related to the Au–Ni/γ-Al_2O_3 catalysts containing 0.27 wt % Au and 0.09 wt % Ni and 0.02 wt % Au and 0.006 wt % Ni in the table).

Note that the conversion of acetylene and the stability of Au–Ni catalysts were much higher than the corresponding characteristics of the analogs, commercially used Pd–Ag catalysts, all other factors being the same. Thus, 70 min after the onset of reaction on the Au–Ni/γ-Al_2O_3 catalyst ([Au] = 0.02 wt %, [Ni] = 0.02 wt %) at 20°C, the conversion of acetylene into ethylene was ~36%, whereas it was only 20% on the prepared Pd–Ag/γ-Al_2O_3 catalyst ([Pd] = 0.02 wt %, [Ag] = 0.02 wt %).

An increase in the reaction temperature from 20 to 64°C on three Au–Ni catalysts containing 0.02% gold resulted in an increase in conversion by 17–39%; in this case, the selectivity and stability of the catalysts remained unchanged.

The dependence of acetylene conversion on gold–nickel catalysts on molar ratio between the supported metals has an extremal character (Fig. 2). As the concentration of gold was increased from 0 to 25 and 50 mol %, the conversion of acetylene increased from 3 to 36 and 69%, respectively. A further increase in the concentration of gold from 50 to 100 mol % resulted in a noticeable decrease in the catalyst activity. The position of a maximum in a curve of the dependence of conversion on the Au : Ni molar ratio was independent of reaction temperature and time.

The synergism of the catalytic effects of Au and Ni in the reaction of acetylene hydrogenation is unusual. The results of a more detailed study on the nature of this synergistic effect with the use of a set of physicochemical techniques for solid surface analysis and quantum-chemical calculations will be published elsewhere.

CONCLUSIONS

Based on the above results, we can make the following conclusions:

(1) The Au–Ni/γ-Al_2O_3 bimetallic catalysts exhibited high activity and selectivity in the reaction of acetylene hydrogenation to ethylene at 20–64°C. The time of their stable operation was no shorter than 12 h.

(2) The Au–Ni/γ-Al_2O_3 catalysts were much superior to the Pd–Ag/γ-Al_2O_3 catalysts with the same total metal contents in terms of activity and stability.

(3) The Au–Ni/γ-Al_2O_3 catalysts exhibited a clearly pronounced synergism in the catalytic effect: the conversion of acetylene on them was higher by about an order of magnitude than that on catalysts based on individual gold or nickel, and it was an extremum function of the Au : Ni ratio.

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