# Selective Hydrogenation of Phenylacetylene into Styrene on Gold Nanoparticles

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**Abstract**—Gold nanoparticles (2–10 nm) supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> exhibit high activity and stability in the hydrogenation of phenylacetylene into styrene in the phenylacetylene—styrene mixture. The selectivity of the catalyst is particle size—dependent: the styrene-to-ethylbenzene molar ratio in the reaction products increases from 2 to 30 as the average gold particle size decreases from 8 to 2.5 nm. The selectivity of phenylacetylene hydrogenation correlates with the selectivity of phenylacetylene adsorption on Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> from the phenylacetylene—styrene mixture.

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The selective removal of acetylenic hydrocarbons from olefins, including the removal of phenylacetylene from commercial styrene, is necessary for obtaining high-quality polymers [1, 2]. At present, this problem is solved by hydrogenation of acetylene derivatives in the presence of bimetallic catalysts containing ultrafine Pd particles and some other metals, such as Ag [3, 4]. However, although these systems are highly active and selective, they are rapidly poisoned by byproducts of the oligomerization of acetylene derivatives. Therefore, it is still a challenging problem to find new approaches to the synthesis of highly efficient and selective hydrogenation catalysts.

The high catalytic activity of Au nanoparticles in a wide variety of processes [5-7] generates interest in catalysis by gold-containing systems. It has recently been found that gold nanocomposites are active in the hydrogenation of 1,3-butadiene, acetylene, propyne, and terminal olefins [8-13]. Therefore, it is of interest to see whether gold nanoparticles are usable in the selective hydrogenation of phenylacetylene in excess styrene. The purpose of this work is to study the dependence of the activity and selectivity of gold nanoparticles on their size in the hydrogenation of phenylacetylene into styrene.

## **EXPERIMENTAL**

## Chemicals

Phenylacetylene (Aldrich, no. 2086451,  $\geq$ 97%) and styrene (Aldrich, no. 2?028?515,  $\geq$ 99.5%) were distilled from P<sub>2</sub>O<sub>5</sub> in an argon atmosphere.

The support was microspherical  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (AO Katalizator, IKT-02-6M brand) with a specific surface area of  $S_{sp} = 138 \text{ m}^2/\text{g}$  and a total pore volume of

 $0.32\ cm^3/g.$  Prior to use,  $\gamma\text{-}Al_2O_3$  was calcined at 350°C for 3 h.

Catalysts were prepared using  $HAuCl_4 \cdot xH_2O$  with an Au content of 49.04 wt % (OAO Aurat, USSR Specifications 6-09-05-1075-89), distilled water, and a 0.1 M aqueous solution of NaOH.

## Preparation of Catalysts

 $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-supported gold particles 2–10 nm in size were formed using an anion adsorption procedure [14]. To obtain the Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, the pH of the aqueous solution of HAuCl<sub>4</sub> was brought to 7.0 by adding sodium hydroxide, an appropriate amount of the support was added to the neutralized solution, and the resulting suspension was stirred at 70°C for 1 h. The catalyst precursor was separated from the mother liquor, washed with distilled water, dried in air for 1 day, and calcined at 300°C in an inert atmosphere for 3 h. The resulting catalysts were stored in dry argon.

# Determining the Composition and Structure of Nanocomposites

The weight percentage of metals in the catalysts was determined by atomic absorption spectrometry on a Hitachi 180-80 spectrometer. For analysis, the metals were washed off the support with a solution of concentrated acids (HCl:  $HNO_3 = 3:1$ ). Electron micrographs of nanocomposites were obtained by transmission electron microscopy (TEM using an LEO912 AB OMEGA instrument with a resolving power of 0.2 nm. For each sample, the size distribution of supported particles was established by statistical processing of data for 300 ones.

# Gas-Phase Hydrogenation of Phenylacetylene–Styrene Mixtures

The catalytic hydrogenation of phenylacetylene– styrene mixtures was carried out in a flow reactor. The catalyst (1 g) was placed on a Schott filter built in a 4-ml Pyrex reactor, which was heated to the preset temperature in a tubular furnace. A liquid mixture (10 mol % phenylacetylene + 90 mol % styrene) was heated in an evaporator to 150°C and was then fed into the reactor. The GHSV of the organic mixture was varied between 200 and 340  $h^{-1}$  and was calculated as

$$F_{\rm GHSV} = \frac{\rho_{\rm prod} V_{\rm prod}}{(\chi_i (C_8 H_6) \times 102 + \chi_i (C_8 H_8) \times 104 + \chi_i (C_8 H_{10}) \times 106)} \times \frac{V_{\rm mol}}{m_{\rm Cat} V_{\rm Cat}} \times \frac{1}{t}$$

where  $\rho_{\text{prod}} = 0.9 \text{ g/ml}$  is the density of the organic fraction of the reaction products,  $V_{\text{prod}}$  is the accumulated volume of organic products (ml),  $V_{\text{mol}} = 34.72 \times 10^3 \text{ ml/mol}$  is the molar volume of the gas at 150°C,  $V_{\text{Cat}}$  is the specific volume of the catalyst ( $V_{\text{Cat}} = 0.885 \text{ ml/g}$  for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), *t* is the accumulation time (h),  $\chi_i$  is the mole fraction of the *i*th product in the final mixture, and  $m_{\text{Cat}}$  is the catalyst weight (g). Hydrogen dried over solid KOH (1.25–1.29 ml/s) was fed into the reactor along with the organic gas mixture. The hydrogen/(styrene + phenylacetylene) molar ratio ranged between 10 and 18. The reaction products were analyzed by GLC on a Kristall-Lyuks 4000 chromatograph (50-m-long Thermon capillary column, constant temperature of 85°C, helium as the carrier gas, flame ionization detector).

The phenylacetylene conversion  $\Delta(C_8H_6)$  was calculated using the formula

 $\Delta(C_8H_6) = (\chi_0(C_8H_6) - \chi_i(C_8H_6))\chi_0(C_8H_6)^{-1} \times 100\%,$ where  $\chi_0(C_8H_6)$  is the mole fraction of phenylacetylene in the organic mixture before the reaction and  $\chi(C_6H_6)$  is the mole fraction of phenylacetylene in the organic mixture *i* h after the initiation of the reaction.

The selectivity of the catalyst at 100% phenylacetylene conversion ( $S_{100}$ ) was calculated as

$$S_{100} = \chi_i(C_8H_8)(\chi_i(C_8H_6) + \chi_i(C_8H_{10}))^{-1}.$$

where  $\chi_i(C_8H_8)$ ,  $\chi_i(C_8H_6)$ , and  $\chi_i(C_8H_{10})$  are the mole fractions of styrene, phenylacetylene, and ethylbenzene, respectively, in the organic mixture after *i*-h-long passing of the reaction mixture through the catalyst bed.

#### Adsorption Measurements

Reactant adsorption was determined by GC from corrected retention volume data for catalyst-packed columns. Chromatographic measurements were carried out on a Kristall Lyuks 4000 chromatograph with a flame ionization detector (column length of 20 mm, inner diameter of 2 mm, oven temperature of 100°C). Sorbate retention parameters, including the sorbate retention time in the chromatographic column ( $t_R$ ) as the time interval between the sample injection and sorbate detection points, the retention time of a nearly nonsorbable substance (methane) ( $t_0$ ), and the corrected retention time of the sorbate ( $t'_R$ ) = ( $t_R - t_0$ ), were determined at a carrier gas (helium) flow rate of

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25 ml/min. Specific corrected retention volumes per unit weight of the catalyst  $(V_r)$  were calculated as

$$V_{\rm r} = (t_{\rm R}' - t_0)/m$$

where *m* is the catalyst weight (g).

The adsorption selectivity for the styrene–phenylacetylene mixture was characterized by the selectivity coefficient  $\alpha_{21} = V_{r2}/V_{r1}$ , where  $V_{ri}$  is the specific corrected retention volume of the *i*th component (the components are numbered in the order of increasing retention times).

## **RESULTS AND DISCUSSION**

## TEM Data

According to the literature [14], the anion adsorption method makes it possible to obtain Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> systems with immobilized gold nanoparticles 2–20 nm in size. In the present work, catalysts with a gold content of  $C_{Au} = 0.018 - 1.8$  wt % were prepared by this method. The catalysts were lilac fine powders.

Typical TEM images of the catalyst samples are shown in Figs. 1–3. The size of supported gold particles (d(Au)) is 5–10 nm for the sample with an Au content of 1.8 wt %, 3–5 nm for [Au] = 0.368 wt %,



**Fig. 1.** TEM image of the Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (1.8 wt %);  $d(\text{Au})_{\text{max}} = 8 \text{ nm}.$ 



**Fig. 2.** TEM image of the Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (0.368 wt %);  $d(Au)_{max}x = 4 \text{ nm.}$ 

and 2–3 nm for [Au] = 0.018 wt %. The particle size distribution maxima ( $d(Au)_{max}$ ) data are given in Table 1. These results are in good agreement with the literature [14].

The following reactions occur in the hydrogenation of the phenylacetylene–styrene mixture [15]:

$$C_6H_5 - C \equiv CH \xrightarrow{H_2} C_6H_5 - CH = CH_2$$
(I)

$$C_6H_5 - C \equiv CH \xrightarrow{H_2} C_6H_5 - CH_2 - CH_3 \qquad (IIa)$$

$$C_6H_5-CH=CH_2\xrightarrow{H_2}C_6H_5-CH_2-CH_3$$
 (IIb)



**Fig. 3.** TEM image of the Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst (0.018 wt %);  $d(\text{Au})_{\text{max}} = 2.5 \text{ nm}.$ 

$$C_6H_5-C \equiv CH \longrightarrow oligomers$$
 (III)

The catalytic hydrogenation of phenylacetylene into styrene (reaction (I)) can be accompanied by the total hydrogenation of the acetylene and olefin derivatives (reactions (IIa) and (IIb)) to ethylbenzene and by phenylacetylene oligomerization (reaction (III)).

In the presence of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support, at 150°C  $\Delta$ (C<sub>8</sub>H<sub>6</sub>) = 4.7% 1 h after the beginning of the run (Table 1). The reaction mixture at the outlet of the reactor contains ethylbenzene (1.8%), the pheny-

Mixture composition, mol % GHSV, h<sup>-1</sup>  $C_{\rm Au},\%$  $d(Au)_{max}, nm$  $S_{100}, \%$ *t*<sub>r</sub>, h  $\chi C_8 H_6$  $\chi C_8 H_8$  $\chi C_8 H_{10}$ 0\* 9.8 0.018 2.5 230 90.2 0 1 0 96.7 3.3 29.3 0 96.7 4 3.3 29.3 0.368 4.0205 0\* 10.2 89.8 0 0.6 0 95.1 4.9 19.4 0 2 95.0 5.0 19.1 0 92.0 8.0 11.6 4 1.8 8.0 200 0\* 9.6 90.4 0 0 79.4 0.5 20.6 3.8 0 70.0 4 30.0 2.3 0 0\* 2.1 97.9 0 340 96.2 1 2.0 1.8

**Table 1.** Molar compositions of the reaction mixture before (\*) and after passing it through an Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst bed at 150°C and 100% phenylacetylene conversion and  $S_{100}$  data

Note:  $C_{Au}$  is the weight percent of gold,  $d(Au)_{max}$  is the maximum gold particle size for the catalyst, and  $t_r$  is the reaction time. The phenylacetylene conversion is  $\Delta(C_8H_6) = (\chi_0(C_8H_6) - \chi_i(C_8H_6))\chi_0(C_8H_6)^{-1}$  100%, and the selectivity of the catalysts at 100% phenylacetylene conversion is  $S = \chi_i(C_8H_8)(\chi_i(C_8H_6) + \chi_i(C_8H_{10}))^{-1}$ .

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Parameter	Catalyst		
	Au(1.8%)/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Au(0.368%)/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	Au(0.018%)/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>
α	1.74	1.89	2.05
$d(Au)_{max}, nm$	8.0	4.0	2.5
S	2.3	11.6	29.3

**Table 2.** Correlation between the hydrogenation selectivity and selective adsorption of phenylacetylene from the reaction mixture on the  $Au/\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts

Note:  $\alpha$  is the phenylacetylene-to-styrene retention volume ratio, *S* is the hydrogenation selectivity after 4-h-long operation for various catalysts at 100% phenylacetylene conversion, and *d*(Au)<sub>max</sub> is the maximum gold particle size in the catalyst.

lacetylene content remains almost unchanged, and the styrene content is lower by 1.7%. The formation of ethylbenzene can be due to the fact that  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> contains traces of hydrogenation-active iron and other metals (according to specifications, IKT-02-6M can contain up to 10<sup>-4</sup> wt % Fe).

The data listed in Table 1 show that the Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts containing 2- to 10-nm gold particles are highly active and stable in the gas-phase hydrogenation of phenylacetylene in styrene at 150°C. At 100% phenylacetylene conversion, the catalyst retains its initial activity for at least 4 h.

The styrene selectivity depends substantially on the average size of the gold particles (Table 1). As the particle size decreases from 8 to 2.5 nm,  $S_{100}$  increases by a factor of 13. It is likely that, in the samples with a lower metal content, the fraction of high-multiplicity reaction sites decreases (the number of substrate coordination points increases) with a decreasing particle size. Let us consider this thesis in greater detail. The species responsible for olefin formation in the hydrogenation of acetylene derivatives are intermediates adsorbed on sites with a multiplicity of 1-2, irrespective of the nature of the metal. On the one hand, alkanes usually form on sites with a multiplicity of 3, whereas oligomers form on sites with a multiplicity of  $\geq 4$  [15]. On the other hand, the proportion of planes (faces) containing high-multiplicity sites decreases sharply as the particle size decreases [16]. Thus, the smaller the Au particle size (and, accordingly, the contribution from the high multiplicity sites to the catalytic processes), the lesser the extent of total hydrogenation and the higher the target product (styrene) selectivity.

Another factor that enhances the selectivity as the Au particle size decreases is the selective adsorption of phenylacetylene from the phenylacetylene–styrene mixture. An essential fact for the selective hydrogenation of acetylenic compounds in the presence of ethylenic compounds is that the latter bind less strongly to palladium- and platinum-based catalyst surfaces and are readily replaced by acetylene homologues [15, 17, 18]. A similar situation takes place in the case of gold particles. Table 2 lists the  $C_8H_6/C_8H_8$  retention volume ratios ( $\alpha$ ) for the catalysts, which characterize the

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phenylacetylene/styrene adsorption selectivity. The largest  $\alpha$  values are observed for the most selective catalyst, which contains the smallest amount of metal and consists of the finest particles. Since the Au content of this catalyst is negligible (the upper estimate of the metal coverage of the support surface is a few tenths of a percent), this result possibly indicates the pronounced adsorption selectivity of the nanosized gold particles toward phenylacetylene. Probably, the adsorption factor contributes substantially to the increase in the selectivity of hydrogenation with a decrease in the gold particle sizes.

## CONCLUSIONS

At 150°C, the Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts are active and stable in the hydrogenation of phenylacetylene into styrene, showing a selectivity of up to 29%.

The styrene selectivity increases with a decreasing Au particle size.

The phenylacetylene hydrogenation selectivity in excess styrene correlates with the selectivity of adsorption of these compounds on Au/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

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