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# Liquid-phase hydrogenation of phenylacetylene to styrene on silica-supported Pd–Fe nanoparticles

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**Bimetallic Pd–Fe/SiO$_2$ catalysts were synthesized and studied in the liquid-phase hydrogenation of phenylacetylene to styrene. The activity (at 0.05–0.1 wt% Pd) and selectivity of the bimetallic system were superior to those of monometallic Pd/SiO$_2$ catalyst.**

$$\mathrm{PhC{\equiv}CH} \xrightarrow[20\,^{\circ}\mathrm{C},\ p(\mathrm{H_2}) = 1\ \mathrm{atm,\ EtOH}]{(0.05\text{–}3\ \mathrm{wt\%})\mathrm{Pd}\text{–}(0.25\text{–}8\ \mathrm{wt\%})\mathrm{Fe/SiO_2}} \mathrm{PhCH{=}CH_2}$$

Hydrogenation of alkynes to alkenes are of great practical significance.[1–6] Pd-based catalysts with a high content of the noble metal (4–9 wt%) are typically used.[6–8] The catalysts on silica support with a lower palladium content (0.2–1.0 wt%) have been proposed recently.[9,10] It is known that the modifications of the Pd-based catalysts by alloying with other metals or metal oxides, including Fe, and the use of some hybrid systems allows one to increase the activity and selectivity of catalysts.[7,11–13] However, data on the effect of Fe on the activity and selectivity of palladium nanoparticles in hydrogenation of phenylacetylene are contradictory.[7,14]

The aim of the present work was to study the influence of composition and preparation conditions of bimetallic Pd–Fe/SiO$_2$ systems on their catalytic activity in the model reaction of liquid-phase hydrogenation of phenylacetylene to styrene.[†]

The synthesized bimetallic Pd–Fe/SiO$_2$ samples, both reduced in a H$_2$ flow at the temperature of Pd precursor reduction and calcined in air at the temperatures of Fe precursor decomposition were active at room temperature and atmospheric H$_2$ pressure. The monometallic FeO$_x$/SiO$_2$ samples under these conditions were inactive, however, introduction of only 0.05 wt% Pd resulted in the detectable activity. Comparison of the initial rates of hydrogenation for the samples with a low Pd content of 0.1 wt% [Figure 1(*a*)] shows that raising the calcination temperature from 250 to 350 °C only slightly affects the activity of these catalysts. The activity of the calcined bimetallic 0.1Pd8Fe catalysts is comparable with that of the monometallic 0.1Pd–H catalyst. The further reduction of sample 0.1Pd8Fe-350C in a H$_2$ flow at 400 °C increased its catalytic activity more than twice [Figure 1(*a*), sample 0.1Pd8Fe-350C-H], and the selectivity to styrene was 83%. The selectivity to styrene at the complete conversion of PhC≡CH was higher on the bimetallic Pd–Fe catalysts as compared to the

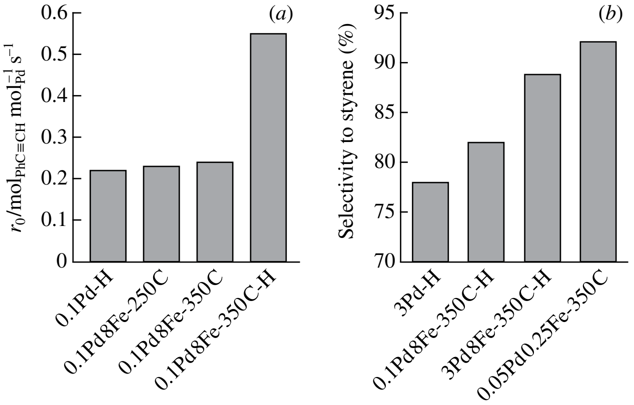

**Figure 1** The influence of (*a*) conditions of thermal treatment on the activity of 0.1Pd8Fe catalysts and (*b*) the composition of catalysts on the selectivity to styrene at the complete conversion of PhC≡CH (carrier – SiO$_2$ HS).

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[†] The bimetallic Pd–Fe catalysts were prepared by incipient wetness impregnation of silica with aqueous solutions of the metal precursors [Pd(NH$_3$)$_4$]Cl$_2$·H$_2$O (pure, 41.42% Pd; Aurat, Russia) and (NH$_4$)$_3$[Fe(C$_2$O$_4$)$_3$]××3H$_2$O (pure, 98%, Acros Organics). The granulated commercial silica[15] with a high (HS) specific surface area ($S$ = 300 m$^2$ g$^{-1}$) and a low (LS) specific surface area ($S$ = 30 m$^2$ g$^{-1}$) were used as supports. The impregnated samples were dried at 60 °C. In some cases, dried samples were calcined at 250–400 °C in air. The dried or calcined samples were reduced in a hydrogen flow at 400 °C for 3 h. The decomposition and reduction temperatures were chosen based on the TG-DTA data and TPR-H$_2$ studies.[15–18] The synthesized catalysts are denoted as $x$Pd$y$Fe-$M$, where $x$ and $y$ are referred to the Pd and Fe loading (wt%), respectively, and $M$ denotes the conditions of thermal treatment (250C–400C correspond to the calcination at 250–400 °C, respectively, H is reduction in H$_2$ at 400 °C). The samples were characterized by TPR-H$_2$ and XRD methods using the described procedures.[15,16] The average particle size was calculated according to the Debye–Scherrer equation.

The catalytic properties of Pd–Fe/SiO$_2$ samples were studied in the laboratory apparatus[19] under the following reaction conditions: the 0.130 M PhC≡CH solution in ethanol, 30 mg of a catalyst, 1 atm H$_2$, room temperature, molar ratio PhC≡CH : Pd = 300–9000 : 1. The reaction products were identified by GC analysis (FID) with undecane as an internal standard. Only styrene and ethylbenzene were detected as reaction products. The catalytic activity was evaluated by the initial rate of PhC≡CH hydrogenation referred to the molar amount of palladium. Comparison of the selectivities was carried out using the values calculated at the complete conversion of PhC≡CH.

**Table 1** The influence of conditions of thermal treatment of Pd–Fe catalysts on the selectivity to styrene and on the initial rate of hydrogenation of phenylacetylene.

| Catalyst | Conditions of thermal treatment | $S^a$ (%) | $r_0^b/\mathrm{mol_{PhC\equiv CH}\ mol_{Pd}^{-1}\ s^{-1}}$ |
|---|---|---|---|
| 3Pd/HS | $H_2$, 400 °C | 78 | 0.33 |
| 3Pd8Fe/HS | $H_2$, 400 °C | 83 | 0.08 |
| | Air, 250 °C | 77 | 0.35 |
| | Air, 400 °C | 86 | 0.31 |
| | Air, 250 °C, $H_2$, 400 °C | 89 | 0.18 |
| 3Pd8Fe/LS | $H_2$, 400 °C | 81 | 0.06 |
| | $H_2$, 400 °C, Ar, 550 °C | 93 | 0.15 |

[a] The styrene selectivity at the complete conversion of PhC≡CH. [b] $r_0$ is the initial rate of hydrogenation calculated at a 30% conversion of PhC≡CH.

monometallic palladium catalyst [Figure 1(*b*)]. The maximum value of the selectivity to styrene of 92% was achieved when the samples with a noble metal content as low as 0.05 wt% were used.

At a higher Pd content, the maximum initial rate of hydrogenation was observed in the presence of the catalyst 3Pd8Fe/HS calcined at 250 °C, and it was comparable with that for 3Pd/HS catalyst (Table 1). The higher calcination temperature of 400 °C resulted only in an increase in the selectivity from 77 to 86%. The reduction of the bimetallic 3Pd8Fe/HS-250C sample in a $H_2$ flow at 400 °C caused a slightly increased selectivity to styrene (89%), but at the same time, a decrease in the activity. The activity was even lower when the dried bimetallic samples were reduced in a $H_2$ flow at 400 °C.

The variations in the activity and selectivity of catalysts are supposed to be due to the differences in the size and composition of Pd and Fe nanoparticles. The phase composition of samples and the primary particle size of supported metal were studied by XRD analysis that revealed the formation of Pd$^0$, α-$Fe_2O_3$ and $Fe_3O_4$ phases after calcination of the precursors of bimetallic 3Pd8Fe samples at 240–260 °C (Figure 2), and the Pd$^0$ average primary particle size was 10 and 20 nm for the samples deposited on HS and LS silica, respectively. The size of Pd$^0$ nanoparticles in the monometallic 3Pd/HS sample after reduction in a $H_2$ flow at 400 °C was 25 nm. Reduction of the bimetallic samples calcined at 240–260 °C in a $H_2$ flow at 400 °C results in the formation of Fe$^0$ nanoparticles of 17–20 nm in size, while the reduction of sample precursor (*i.e.*, sample dried at 60 °C) under the same conditions leads to amorphous (X-ray) Fe$^0$ phases (Figure 2). The appearance of the intense Fe$^0$ line and the shift of the Pd$^0$ line on the XRD pattern of the sample reduced after annealing in purified argon at 550 °C provides evidence for the reduction of Fe$^{n+}$ to Fe$^0$ and formation of nanoparticles of a solid solution $Pd_{1-x}Fe_x$.

Several overlapping peaks of hydrogen consumption can be recognized on the TPR profiles of the bimetallic Pd–Fe samples calcined at 250 °C (Figure 3) that show the reduction of different $Fe_xO_y$ phases. The calculated total H : Fe atomic ratio (Figure 3) approached the value for reduction of $Fe_2O_3$ to FeO for the samples 8Fe/HS-240C and 0.1Pd8Fe/HS-250C, whereas it was more than two times larger for the sample 3Pd8Fe/HS-250C indicating partial reduction to Fe$^0$.

Hydrogen consumption by the bimetallic samples with both high and low Pd content was observed below 350 °C, *i.e.* before reaching the temperature of reduction of Fe oxides in the monometallic sample $FeO_x/SiO_2$ (Figure 3), indicating strong interaction between Fe oxide and Pd species and promoting effect of Pd$^0$ on the reduction of $Fe_xO_y$. The absence of both peaks of hydrogen consumption at low temperatures and the minimum of hydrogen release at 50–70 °C, which are characteristic of Pd$^0$ nanoparticles and β-PdH phase and were observed on the TPR curve of the referred monometallic Pd/$TiO_2$ sample[20] (Figure 3), indicated the absence of pure Pd$^0$ nanoparticles and incorporation of Fe in Pd$^0$ nanoparticles with formation of Pd–Fe–O and Pd–Fe alloy phases of different composition[21,22] at the step of calcination.

In conclusion, the catalytic activity in hydrogenation of phenylacetylene and selectivity to styrene depends on the composition and conditions of thermal treatment of Pd–Fe/$SiO_2$ systems and, therefore, on the state of Pd and Fe in the samples. The formation of the X-ray amorphous Pd–Fe alloy in the reduced 3Pd8Fe/LS sample causes a significant drop in activity of the sample compared to the monometallic one. However, recrystallization sintering of nanoparticles of the alloy during annealing in argon at 550 °C significantly increases the activity and selectivity (93%) of the formation of styrene that is higher than that in the case of monometallic palladium catalyst (77%), although the initial rate

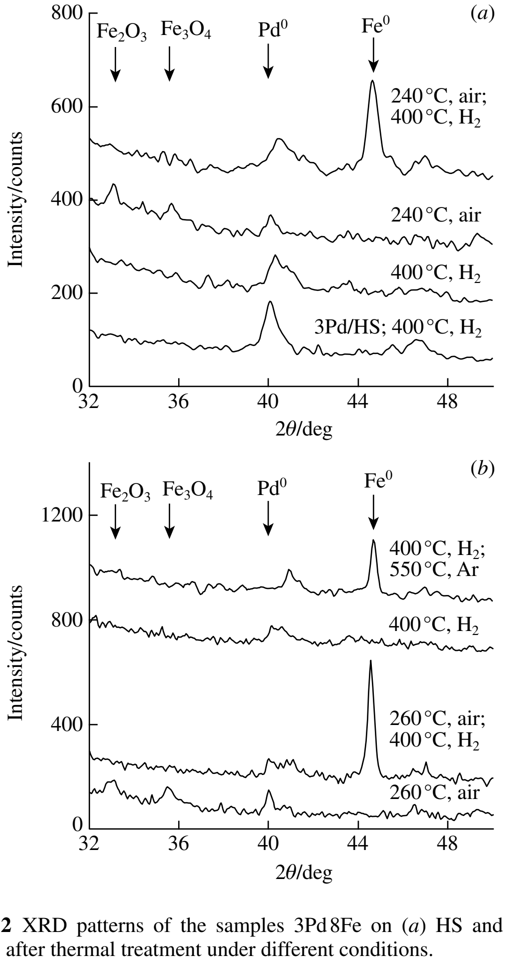

**Figure 2** XRD patterns of the samples 3Pd8Fe on (*a*) HS and (*b*) LS supports after thermal treatment under different conditions.

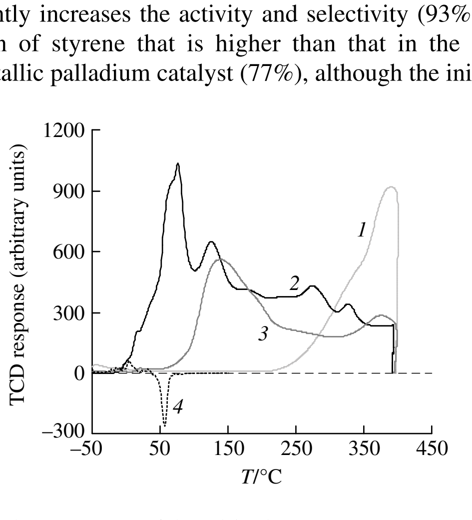

**Figure 3** The TPR curves of the calcined (*1*) 8Fe/HS-240C, H : Fe = 0.88, (*2*) 3Pd8Fe/HS-250C, H : Fe = 1.90, (*3*) 0.1Pd8Fe/HS-250C, H : Fe = 0.84 and (*4*) 1Pd/$TiO_2$ samples.

of the process using this bimetallic catalyst is lower. It is likely that increase in the selectivity of Pd–Fe catalysts reduced in hydrogen after calcination is associated with the reduction of iron oxides and formation of alloys based on Pd. As a result, the obtained bimetallic Pd–Fe/$SiO_2$ catalysts with a Pd content of only 0.05–0.1 wt% are more effective than the monometallic Pd/$SiO_2$ catalysts with the same Pd content at room temperature and atmospheric $H_2$ pressure. The prepared catalysts will be further tested for hydrogenation of carbon dioxide.

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