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New High-Selectivity Hydrogenation Catalysts Prepared from Bimetallic Acetate Complexes

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Abstract—The catalytic properties of new Pd–Zn/Al_2O_3 catalysts in selective acetylene hydrogenation in an acetylene–ethylene mixture at 30–120°C and atmospheric pressure are reported. The catalysts prepared from the bimetallic complex Pd–Zn$(OOCMe)_4(OH_2)$ are much more selective than the catalysts prepared by simultaneously supporting the homonuclear complexes $Pd_3(OOCMe)_6$ and $Zn(OOCMe)_2 \cdot 2H_2O$. It is demonstrated by diffuse reflectance IR spectroscopy of adsorbed CO that the heat treatment of the supported bimetallic complex at 250°C in flowing H_2 yields a Pd–Zn alloy on the surface. It is this alloy that ensures the high selectivity of the Pd–Zn/Al_2O_3 catalysts.

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The selective hydrogenation of acetylene into ethylene in acetylene–ethylene mixtures is the key reaction in the industrially important process of catalytic acetylene removal from ethylene for polyethylene production [1]. Since acetylene is very poisonous to ethylene polymerization catalysts, its concentration in the ethylene feedstock should not exceed 5 ppm [2, 3].

The hydrogenation of acetylene and its homologues is usually carried out on Pd/Al_2O_3 catalysts [4]. The most important parameter of this reaction is the ethylene selectivity ($S_{C_2H_4}$). For a high ethylene selectivity, acetylene adsorption on the active sites of the catalyst must be sufficiently strong to prevent ethylene adsorption on the same sites [5]. The acetylene hydrogenation selectivity is also favored by factors hampering ethylene adsorption from ethylene–acetylene mixtures. These include the reversible poisoning of the catalyst with sulfur-containing compounds, CO_x and NO_x [6–8]. These compounds reduce the total number of hydrogenation sites, but the surface remains completely covered with acetylene even when its concentration in the gas mixture is low. However, these compounds are poisonous to the catalysts used in subsequent ethylene polymerization.

For this reason, the selectivity of the hydrogenation of ethylene–acetylene mixtures in industry is usually raised in a different way, namely, by promoting the supported palladium catalyst with a second metal (Zn, Ag) [9–11]. These promoted catalysts are prepared by successive or simultaneous impregnation of a support with solutions of individual metal salts. The main drawback of this technique is that it is difficult to bring these compounds into intimate contact and then obtain bimetallic alloy particles by reductive treatment of the catalyst.

Here, we report a new approach to the preparation of supported bimetallic hydrogenation catalysts. This approach is based in the use of the recently synthesized and structurally characterized heterobimetallic acetate complex Pd-Zn$(OOCMe)_4(OH_2)$ (**I**) [12] as the catalyst precursor. An advantage of this approach is that the Pd^{II} and Zn^{II} atoms in the structure of this complex are strongly bonded by four acetate bridges [12, 13]. Owing to this structure of the precursor complex, it would be expected that the close contact between the palladium and zinc atoms will not be broken by catalyst supporting and reductive pretreatment. This would be favorable for the formation of a bimetallic structure on the catalyst surface. Earlier, we discovered by X-ray diffraction and X-ray absorption fine-structure (XAFS) spectroscopy that the reduction of carbon-supported complex **I** with hydrogen at 150–250°C affords a Pd–Zn (1 : 1) heterometallic alloy [13].

EXPERIMENTAL

Catalyst Preparation

For obtaining supported monometallic and bimetallic palladium catalysts with a metal content of 0.04–0.93%, an Al_2O_3 support was loaded with the active component by incipient-wetness impregnation with a methanolic solution of $Pd_3(OOCMe)_6$, $Zn(OOCMe)_2 \cdot 2H_2O$, or Pd–Zn$(OAc)_4(OH_2)$ (**I**). The support was α-Al_2O_3 (S_{sp} = 8.1 m^2/g) for low-percentage catalysts and γ-Al_2O_3 (S_{sp} = 76 m^2/g, Puralox TH 500/80, Sasol) for high-percentage catalysts. All complexes were synthesized as described in [12]. Bimetallic catalysts with various palladium and zinc contents were prepared by coimpregnation. The com-

Table 1. Composition and designations of the catalysts

Designation	Catalyst	Active component content, %		Support (specific surface area)	Precursor complex	Preparation method
		Pd	Zn			
A	Pd/Al_2O_3	0.93	–	γ-Al_2O_3 (76 m^2/g)	$Pd_3(OOCMe)_6$	Impregnation
B	$Pd–Zn/Al_2O_3$	0.93	0.58		$PdZn(OOCMe)_4(OH_2)$	Impregnation
C	$Pd–Zn/Al_2O_3$	0.93	0.58		$Pd_3(OOCMe)_6$ + $Zn(OOCMe)_2 \cdot 2H_2O$	Coimpregnation
D	Pd/Al_2O_3	0.04	–	α-Al_2O_3 (8.1 m^2/g)	$Pd_3(OOCMe)_6$	Impregnation
E	$Pd–Zn/Al_2O_3$	0.04	0.025		$PdZn(OOCMe)_4(OH_2)$	Impregnation
F	$Pd–Zn/Al_2O_3$	0.04	0.025		$Pd_3(OOCMe)_6$ + $Zn(OOCMe)_2 \cdot 2H_2O$	Coimpregnation

positions and designations of the catalysts are presented in Table 1.

Catalytic Tests

Catalyst samples were tested in the selective hydrogenation of an acetylene–ethylene mixture containing 1.26 vol % C_2H_2 and 98.74 vol % C_2H_4. The tests were performed in a flow reactor at 1 atm and 20–120°C. The catalyst bed temperature was monitored with a chromel–alumel thermocouple and was maintained using a temperature controller with an accuracy of ±1 K. The working mixture was diluted with hydrogen so that $H_2 : C_2H_2 = 2 : 1$ mol/mol. The GHSV of the acetylene–ethylene mixture was varied in the 3000–45000 h^{-1} range. The catalyst was preheated to 80°C at a rate of 5 K/min in flowing argon and was held at this temperature for 2 h. Next, the catalyst was reduced with flowing H_2 at 250°C for 1 h and was cooled in flowing argon to room temperature in order to decompose the resulting palladium hydride [13, 14]. The reactant and product concentrations were determined by GLC.

The acetylene conversion ($X_{C_2H_2}$) was calculated as the ratio of the total amount of reacted acetylene (ΔC_2H_2) to the amount of acetylene in the feed. The selective hydrogenation of acetylene in excess ethylene involves the following reactions:

$$C_2H_2 + H_2 \longrightarrow C_2H_4, \quad \text{(I)}$$

$$C_2H_4 + H_2 \longrightarrow C_2H_6. \quad \text{(II)}$$

Reaction (I) is the desired reaction, and reaction (II) is a side reaction. The latter is undesired because it wastes H_2 and reduces the ethylene concentration. In view of this, the selectivity of the catalyst (S_{Cat}) was estimated as

$$S_{Cat} = (\Delta C_2H_2)/(\Delta C_2H_2 + \Delta C_2H_6),$$

where ΔC_2H_2 is the amounted of reacted acetylene and ΔC_2H_6 is the amount of the resulting ethane.

The activity of catalysts in selective acetylene hydrogenation ($A_{C_2H_2}$) was calculated as the amount of reacted acetylene per unit weight of palladium per unit time. The formation rates of ethylene ($w_{C_2H_4}$) and ethane ($w_{C_2H_6}$) were derived from the amount of reacted acetylene (ΔC_2H_2) and the amounts of the resulting ethylene (ΔC_2H_4) and ethane (ΔC_2H_6), respectively, per unit time.

IR Spectroscopic Characterization of Catalysts

Diffuse reflectance IR spectra were obtained on a Nicolet Protégé 460 FTIR spectrometer using the technique described in [15]. Catalyst powders were placed in a tube with a KBr window. The probe molecule was CO at an equilibrium pressure of 5 Torr. CO adsorption was carried out at room temperature, followed by desorption in vacuo at room temperature and at 100°C for 1 h. IR spectra were recorded at room temperature in the 6000–400 cm^{-1} range with 4-cm^{-1} resolution. The number of scans was 200. Pd/Al_2O_3 and $Pd–Zn/Al_2O_3$ catalysts were examined after being heat-treated at 120°C in vacuo and at 250°C in flowing hydrogen. After reduction with H_2, the catalysts were heat-treated in vacuo at the same temperature to decompose the resulting palladium hydride [14].

RESULTS AND DUSCUSSION

Experimental data demonstrated that the high- and low-percentage catalysts show similar catalytic activities in acetylene hydrogenation (Figs. 1a, 2a, Table 2). For all catalysts examined, the acetylene conversion increases with increasing temperature. The sample **B** (0.93% Pd–0.58% Zn/Al_2O_3), prepared from bimetallic complex **I**, affords a higher acetylene conversion than the samples **A** and **C**.

An analysis of selectivity versus acetylene conversion data (Fig. 1b, Table 2) for high-percentage catalysts (0.93% Pd, 0.58% Zn) shows that the initial monometallic catalyst 0.93% Pd/Al_2O_3 (**A**), prepared by conventional impregnation, is less selective than the bimetallic catalysts. The maximum S_{Cat} value for

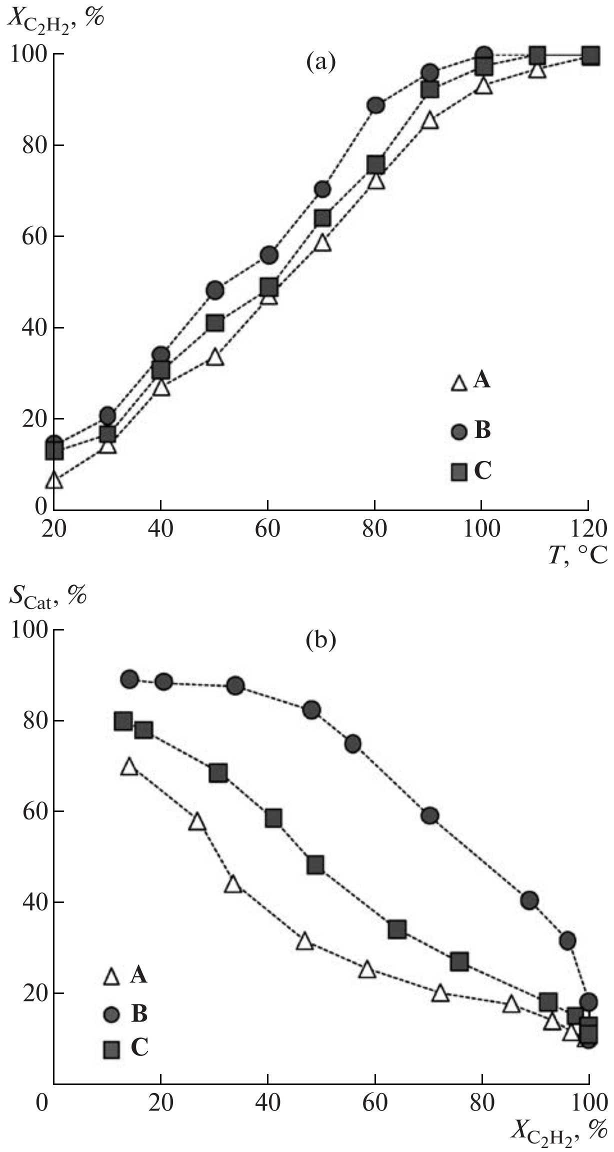

Fig. 1. (a) Acetylene conversion versus temperature and (b) the selectivity of the catalyst versus the acetylene conversion for selective acetylene hydrogenation over the catalysts **A** (0.93% Pd/Al_2O_3), **B** (0.93% Pd–0.58% Zn/Al_2O_3, impregnation with a solution of complex **I**), and **C** (0.93% Pd–0.58% Zn/Al_2O_3, coimpregnation with $Pd(AcO)_2$ and $Zn(OAc)_22H_2O$ solutions). GHSV = 45000 h^{-1}.

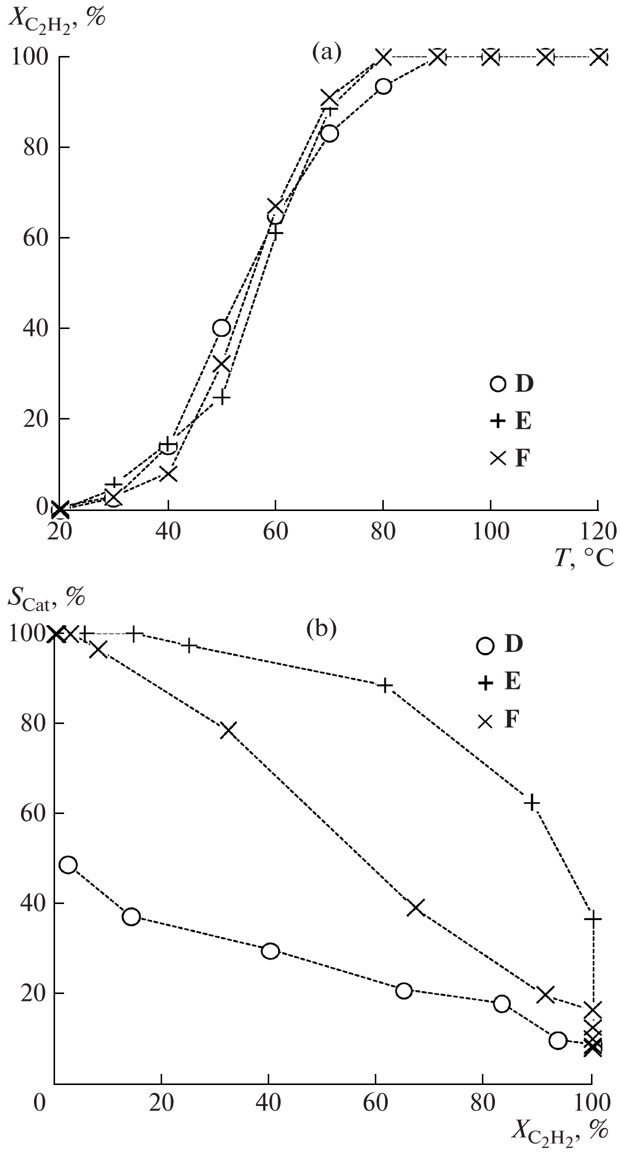

Fig. 2. (a) Acetylene conversion versus temperature and (b) the selectivity of the catalyst versus the acetylene conversion for selective acetylene hydrogenation over the catalysts **D** (0.04% Pd/Al_2O_3), **E** (0.04% Pd–0.025% Zn/Al_2O_3, impregnation with a solution of complex **I**), and **F** (0.04% Pd–0.025% Zn/Al_2O_3, coimpregnation with $Pd(OAc)_2$ and $Zn(OAc)_22H_2O$ solutions). GHSV = 3000 h^{-1}.

this sample is ~70% at ~15% acetylene conversion (Fig. 1b). The promotion of the Pd/Al_2O_3 catalyst with zinc raises its selectivity. For example, the selectivity of the catalyst **B** at ~15% acetylene conversion is ~89%. The sample **C**, prepared by coimpregnation of alumina with the monometallic complexes $Pd(OOCMe)_2$ and $Zn(OOCMe)_2$, is characterized by a smaller S_{Cat} value than **B**. The selectivity of **C** at 15% acetylene conversion is ~78%. As the acetylene conversion increases, the selectivity of this catalyst decreases to come close to the selectivity of **A** at high conversions. For example, at an acetylene conversion of ~80%, the selectivity of the monometallic catalyst **A** is ~18% and the selectivity of **C** is ~22%. For the catalyst **B**, the calculated selectivity is 55%.

A similar trend is observed for the low-percentage catalysts, whose metal contents (0.04% Pd, 0.025% Zn) are similar to those of the commercial catalysts for selective acetylene hydrogenation [16–18]. The sample **D**, prepared from the complex $Pd_3(OOCMe)_6$, shows a rather low selectivity. The maximum selectivity of this sample is 49%. The introduction of Zn into this catalyst markedly enhances its selectivity (Fig. 2b), as in the case of the high-percentage samples **B** and **C** (Fig. 1b). The highest selectivity was observed for the catalyst **E**, which was prepared from heterobimetallic complex **I**. While the selectivity of the monometallic catalyst **D** is ~38% at ~14% acetylene conversion, the sample **E**, prepared from bimetallic complex **I**, shows a selectivity of 98% (Fig. 2b). The catalyst **F**, prepared by impregnation with $Pd_3(OOCMe)_6$ and $Zn(OOCMe)_2$ solutions, exhibits a lower selectivity than **E** (Table 2).

The high selectivity of the catalysts **B** and **E** and the small S_{Cat} values observed for the monometallic catalysts **A** and **D** and for the bimetallic samples **C** and **F** can be explained in terms of ethylene hydrogenation rate variation. It follows from Figs. 3 and 4 that the ethylene formation rate initially increases with increasing temperature for all of the samples examined. It passes through a maximum at 40–60°C (for the monometallic samples **A** and **D** and for the samples **C** and **F**, prepared by coimpregnation) or 70°C (for the catalysts **B** and **E**, prepared from bimetallic complex **I**) and then falls off. At the same time, apparently because of the decreasing acetylene concentration in the mixture, the ethane concentration grows sharply. This is explained by the acceleration of ethylene hydrogenation into ethane.

These regularities are typical of palladium catalysts on conventional supports (Al_2O_3, SiO_2, C), and they are explained by the fact that, at high concentrations, acetylene blocks the palladium surface, thereby preventing the nonselective hydrogenation of ethylene [19–21]. As the proportion of C_2H_2 in the mixture decreases, acetylene leaves the Pd surface and the ethylene hydrogenation rate increases greatly as a result. It is likely that, in the case of heterobimetallic complex **I** used as the precursor (samples **B** and **E**), acetylene is adsorbed more strongly on the active sites of the catalysts, thus preventing ethylene adsorption. This is responsible for the low ethane formation rate and high ethylene selectivity observed for **B** and **E**.

The high selectivity of the catalysts **B** and **E** and the stronger acetylene adsorption on their active sites are most likely due to the formation of bimetallic alloys of Pd with the inactive metal [11, 22, 23]. Earlier, we demonstrated by EXAFS spectroscopy and XRD that heat treatment of complex **I** in flowing H_2 at 150–250°C causes the reduction of zinc to the metallic state and subsequent formation of a Pd–Zn alloy [13, 24]. The promotion of the Pd/Al_2O_3 catalyst with a second metal removes the partial positive charge from the ultrafine palladium particles and thus reduces their activity toward olefin molecules [23]. This makes the catalyst more selective toward ethylene.

The state of Pd and Zn in the catalysts was studied by IR spectroscopy of adsorbed carbon monoxide. Figure 5 shows the spectra recorded upon CO adsorption and desorption for the samples **A** and **B** (0.93% Pd/Al_2O_3 and 0.93% Pd–0.58% Zn/Al_2O_3, respectively) prepumped at 120°C. After CO adsorption at room temperature, the spectra show absorption bands due to CO at 2131–2133 and 2090–2098 cm^{-1}, as well absorption bands at 1967 and 1932 cm^{-1}. According to the literature [25, 26], CO adsorption on alumina-supported palladium catalysts gives rise to three bands due to linear adsorption species: 2170–2145 cm^{-1} for Pd^{2+}–CO, 2135–2110 cm^{-1} for Pd^{+}–CO, and 2100–2050 cm^{-1} for Pd^0–CO. In addition, the IR spectra show bands in the 2000–1800 cm^{-1} range, which are due to the bridging CO species adsorbed on two or three palladium cationic or neutral metal sites [25, 26]. During CO desorption at room temperature, the IR spectra of the monometallic and bimetallic catalysts indicate a sharp weakening of the bands from the linear CO adsorption species, which disappears completely upon pumping at 100°C (Fig. 5).

Table 2. Acetylene conversion and the activity and selectivity of the high-percentage (**A**, **B**, **C**)* and low-percentage (**D**, **E**, **F**)** catalysts in selective acetylene hydrogenation

Catalyst	$X_{C_2H_2}$, %***	$A_{C_2H_2} \times 10^3$, mol (μmol Pd)$^{-1}$ s^{-1}***	S_{Cat}, %***
A	47.2	0.033	31.3
B	56.1	0.039	74.4
C	49.1	0.034	48.1
D	64.9	0.0059	21.2
E	67.1	0.0064	88.6
F	61.2	0.0061	39.4

Notes: * Metal content of the samples: 0.93% Pd, 0.58% Zn.
** Metal content of the samples: 0.04% Pd, 0.025% Zn.
*** $T = 60$°C.

Our earlier XAFS data on the electronic state and local structure of palladium in these catalysts [13, 24] demonstrate that heat treatment at 120°C does not change the electronic state or coordination sphere of Pd. Therefore, the observed IR absorption bands are likely due to the stretching vibrations of the CO molecules adsorbed on Pd^{2+} cations of the acetate complex in linear and bridging forms, respectively. Note, however, that CO adsorption on oxidized palladium-containing samples can cause palladium reduction to Pd^+ or Pd^0 [25, 26]. In the case of the destructive interaction of CO with the monometallic and bimetallic acetate complexes, which causes Pd reduction, the bands at 2131–2133 and 2090–2098 cm^{-1} can be assigned to the linear CO adsorption species on Pd^+ and Pd^0, respectively.

The diffuse reflectance IR spectra of adsorbed CO for the catalysts **A** (Pd/Al_2O_3) and **B** ($Pd–Zn/Al_2O_3$) reduced at 250°C are presented in Fig. 6. After CO

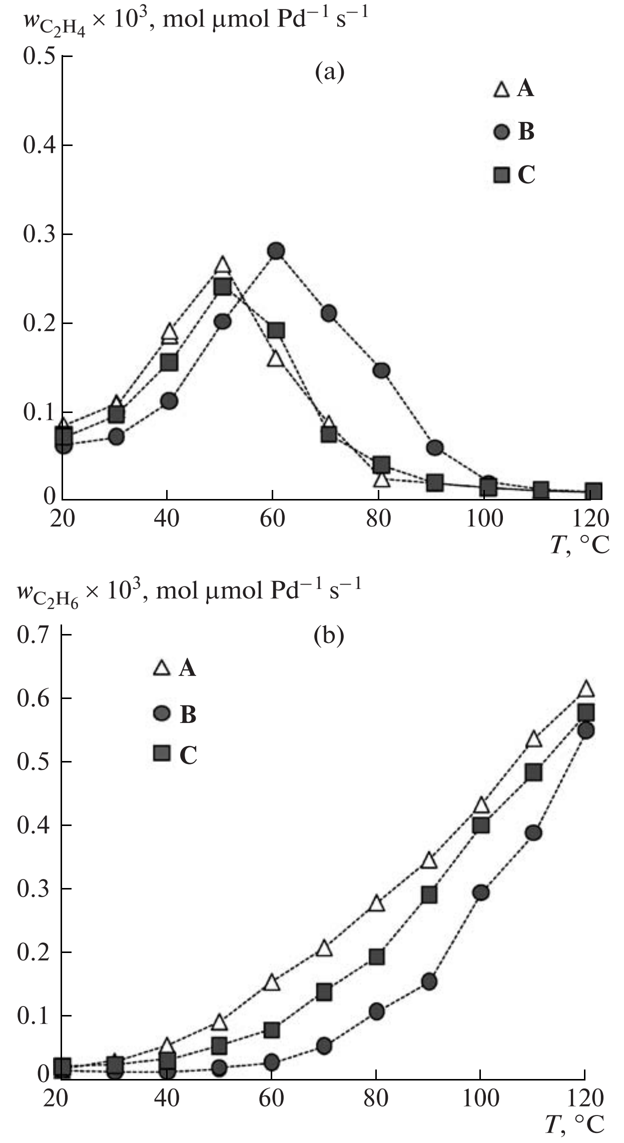

Fig. 3. Effect of temperature on the (a) ethylene and (b) ethane formation rates in selective acetylene hydrogenation over the catalysts **A**, **B**, and **C**. The compositions of the catalysts are given in Table 1.

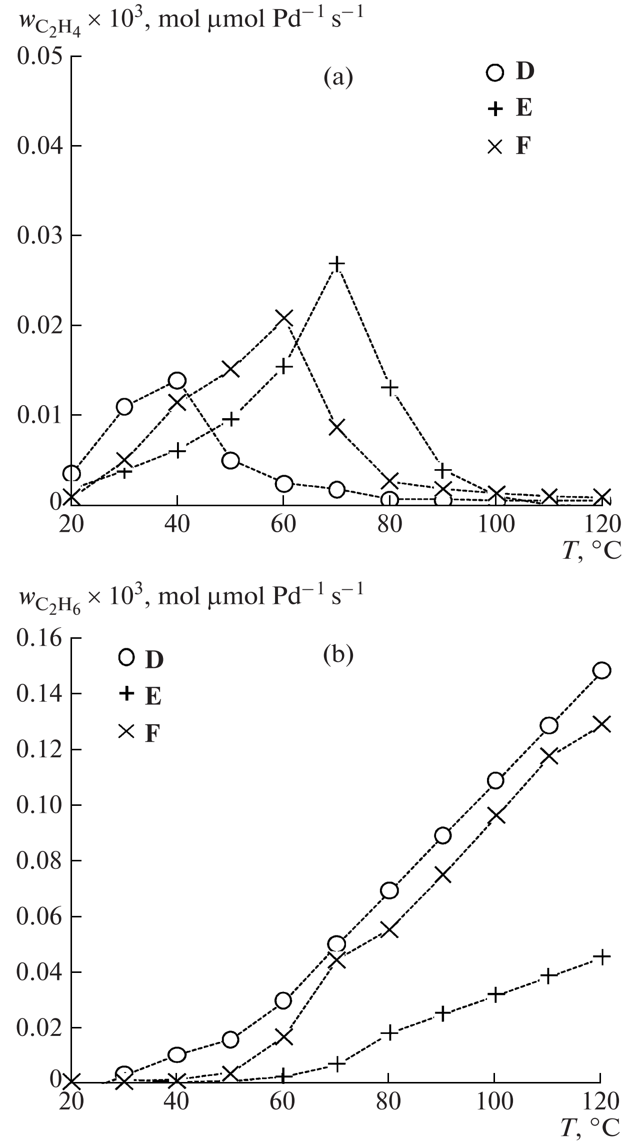

Fig. 4. Effect of temperature on the (a) ethylene and (b) ethane formation rates in selective acetylene hydrogenation over the catalysts **D**, **E**, and **F**. The compositions of the catalysts are given in Table 1.

adsorption at room temperature, the spectra show the absorption bands of CO at 2065 cm^{-1} (for Pd/Al_2O_3), 2078 cm^{-1} (for Pd–Zn/Al_2O_3), and 1940 cm^{-1} (for both catalysts), whose intensity decreases during CO desorption at room temperature. When treated with hydrogen at 250°C, zinc in Pd–Zn/Al_2O_3 undergoes reduction to the metallic state owing to hydrogen activation on Pd possibly followed by hydrogen spillover from palladium metal to zinc, thus yielding a Pd–Zn alloy [13, 24]. The formation of a Pd–Zn alloy is proved by the shift of the stretching frequency of the linear CO adsorption species [27]. The 2065 cm^{-1} band in the spectrum of the bimetallic catalyst, as compared to the band at 2078 cm^{-1}, characterizes CO adsorption on palladium metal sites with a higher electron density. Note that the increase in the electron density on metallic palladium as a result of Pd–Zn alloy formation was also indicated by Pd*K* XANES spectra [13, 24].

Along with the blue shift of the absorption band of the linear CO adsorption species, another evidence of Pd–Zn alloy formation is the change in the intensity ratio between the bands due to the linear and bridging CO adsorption species [28–30]. Upon the formation of a palladium-containing alloy, the bands characterizing CO bridges adsorbed on palladium weaken markedly or disappear [27].

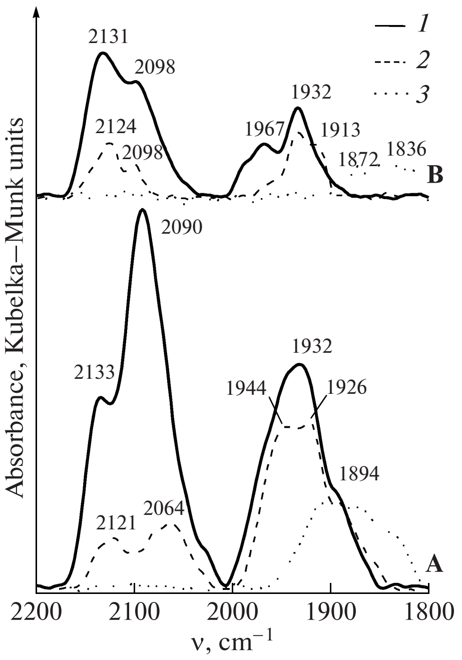

Fig. 5. Diffuse reflectance IR spectra of CO adsorbed at room temperature on the catalysts **A** and **B** pre-heat-treated at 120°C in vacuo: (*1*) adsorption, (*2*) desorption at room temperature, and (*3*) desorption at 100°C.

Figure 7 shows the IR spectra of CO adsorbed on the Pd/Al_2O_3 and Pd–Zn/Al_2O_3 catalysts dehydrated at 120°C in vacuo and then heat-treated in H_2 at various temperatures. Clearly, the intensity ratios between the linear and bridging CO adsorption species in the spectra of Pd–Zn/Al_2O_3 and Pd/Al_2O_3 are the same until the reduction temperature is raised to 250°C. At this temperature, the band of bridging CO weakens, which can be explained by the formation of an alloy in the bimetallic sample [27].

Thus, the above experimental data suggest that the use of the heterobimetallic complex Pd–Zn$(OOCMe)_4(OH_2)$ as the precursor affords an efficient bimetallic alloy catalyst for acetylene hydrogenation. The high selectivity of this catalyst is due to the formation of a Pd–Zn alloy upon the heat treatment of the catalyst at 250°C in flowing H_2. This was established earlier by XANES, EXAFS, and XRD and was proved by IR spectroscopy of adsorbed CO. The formation of the Pd–Zn bimetallic alloy counterbalances the partial charge that appears on the ultrafine palladium particles. As a consequence, these particles become less active toward olefin molecules, acetylene adsorbs more strongly on the active sites of the catalyst to prevent ethylene adsorption, and the active sites responsible for ethane formation are blocked. This results in an increase in the ethylene selectivity.

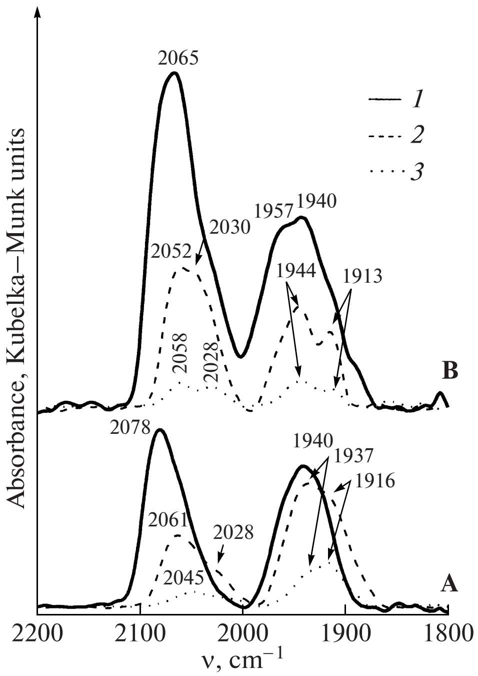

Fig. 6. Diffuse reflectance IR spectra of CO adsorbed at room temperature on the catalysts **A** and **B** pre-heat-treated at 250°C in H_2: (*1*) adsorption, (*2*) desorption at room temperature, and (*3*) desorption at 100°C.

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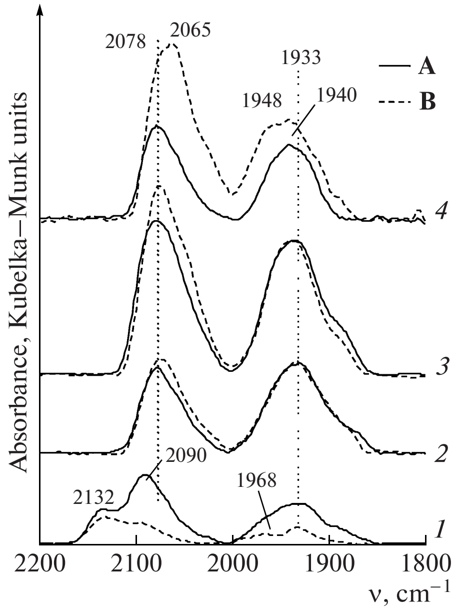

Fig. 7. Diffuse reflectance IR spectra of CO adsorbed at room temperature on the catalysts **A** and **B** pretreated in various ways: (*1*) vacuum, 120°C; (*2–4*) H_2, 50, 150, and 250°C, respectively.

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