

Liquid-Phase Hydrogenation of Acetylene on the Pd/Sibunit Catalyst in the Presence of Carbon Monoxide

N. B. Shitova, D. A. Shlyapin, T. N. Afonasenko, E. N. Kudrya,
P. G. Tsyrul'nikov*, and V. A. Likhlobov

Institute of Hydrocarbon Processing, Siberian Branch, Russian Academy of Sciences, Omsk, 644040 Russia

* e-mail: tsyr@ihcp.oscsbras.ru

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Abstract—The liquid-phase catalytic hydrogenation of acetylene into ethylene in the presence of CO over palladium supported on the graphite-like material Sibunit has been investigated. Carbon monoxide is an effective modifier of the selective hydrogenation process, exerting its effect by competing with acetylene and ethylene for chemisorption sites on the palladium surface. Under the optimum conditions ($T = 90^\circ\text{C}$; N -methylpyrrolidone solvent; feed consisting of 2 vol % C_2H_2 , 90 vol % H_2 , and He balance), the introduction of 2 vol % CO ensures a high ethylene selectivity of $89.6 \pm 1.5\%$ at an acetylene conversion of $95.8 \pm 1.3\%$, with the acetylene converted into hydroooligomers taken into account.

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The present-day technologies for the oxidative pyrolysis of C_1 – C_3 hydrocarbons yield a mixture consisting of hydrogen (up to 70%), acetylene (up to 15%), CO (up to 10%), and small amounts of other compounds (CO_2 , H_2O) [1]. Because of the very large $\text{H}_2 : \text{C}_2\text{H}_2$ ratio in the resulting mixture, the direct gas-phase hydrogenation of acetylene mainly yields ethane rather than ethylene, and this is unacceptable from the practical standpoint. For this reason, some companies are developing a liquid-phase catalytic acetylene hydrogenation process in which a high ethylene selectivity can be attained owing to the large difference between the solubilities of acetylene, ethylene, and hydrogen [2]. We failed to find any articles dealing with liquid-phase acetylene hydrogenation over heterogeneous catalysts in the past 10 years' literature, except for a few patents. In the comprehensive reviews by Borodzinski and Bond [3, 4], published in 2006 and 2008, the latest study on liquid-phase hydrogenation dates back to 1995. Asplund et al. [5] and Edvinsson et al. [6] demonstrated that CO at a low concentration of 400 ppm in the gas phase decreases, by 50%, the rate of liquid-phase acetylene hydrogenation in the C_2H_2 (3%) + C_2H_4 (28%) + H_2 (6 or 11%) + nitrogen (balance) mixture in *n*-heptane at a total pressure of up to 2 MPa. Raising the CO concentration to 1200 ppm completely terminates the hydrogenation process. The authors attribute the inhibiting effect of CO to the blocking of hydrogen adsorption sites. Note that the catalyst in those studies was palladium supported on α - Al_2O_3 honeycomb monoliths with an α - or γ - Al_2O_3 secondary support. The active element (palladium) content of the catalyst was as low as 0.04 wt %; however, the palladium content per unit mass of the sec-

ondary support was greater by approximately one order of magnitude. Since the specific surface area of the catalyst was as small as 7–40 m^2/g , the degree of dispersion of palladium was comparatively low, 7–40%, depending on the precursor.

Earlier, Sokol'skii [7] demonstrated that the most active and most selective catalysts for liquid-phase acetylene hydrogenation to ethylene are supported palladium catalysts; however, the role of CO remained unclear. Gas-phase acetylene hydrogenation has been investigated rather extensively because of the use of this reaction in industrial-scale removal of acetylene from ethylene.

Here, we report the regularities of liquid-phase catalytic acetylene hydrogenation over palladium supported on the carbon material Sibunit (described in an earlier publication [9]) in the presence of CO. As distinct from conventional supports (e.g., Al_2O_3), Sibunit does not have acid sites responsible for acetylene oligomerization into products (oils) interacting with palladium and reducing its catalytic activity.

EXPERIMENTAL

Pd/Sibunit catalysts were synthesized using palladium nitrate (whose synthesis is described elsewhere [10]) as the precursor. The support was Sibunit with a specific surface area of 320 m^2/g . A portion of Sibunit (25 g, 0.1–0.25 mm size fraction) was placed in a 200-ml evaporating dish, and 50% HNO_3 (40 ml) was added. The mixture was evaporated in a water bath under stirring until nitrogen oxide evolution stopped and the support was air-dry. The Sibunit treated in this way was held at 120°C for 8 h to remove the residual

water and nitric acid. Next, an aqueous $\text{Pd}(\text{NO}_3)_2$ solution at an appropriate concentration was added to a portion of the resulting Sibunit. The solution turned colorless, indicating palladium nitrate chemisorption on the support. Thereafter, the $\text{Pd}(\text{NO}_3)_2/\text{Sibunit}$ slurry was evaporated in a water bath under stirring until air-dry. The product was dried at 120°C for 2 h and was then placed in a glass reactor and reduced with flowing hydrogen at 200°C for 3 h. The resulting catalyst contained 0.5 wt % Pd (under the assumption that the entire palladium nitrate was adsorbed). It was stored in an argon atmosphere in a desiccator.

Catalytic activity was measured at 50 to 90°C and atmospheric pressure using a temperature-controlled shaker-type flow reactor. The gaseous feed included acetylene (2 vol %), hydrogen (90 vol %), CO in some cases, and helium (balance). In all runs, the flow rate of the gas mixture in the reactor was 100 ml/min. The time on stream was 350–450 min.

Measurements were taken while vigorously shaking the catalyst suspension (≥ 300 shakes per minute) so as to ensure that the reaction rate is independent of the shaking vigor. Under these conditions, the rate of dissolution of the gas-phase components (C_2H_2 , C_2H_4 , H_2) in the liquid was far above their conversion rate. The feed composition was controlled by varying the acetylene, hydrogen, helium, and carbon monoxide flow rates with flow control valves built in a Khromos GKh-1000 chromatograph. A catalyst sample (0.1–0.6 g) with a particle size of 0.1–0.25 mm and 8–20 ml of the solvent (*N*-methylpyrrolidone, bp 150°C) were placed in a 70-ml reactor, and an H_2 –He mixture was passed through the reactor under shaking. Once the preset temperature was reached (which took about 20 min), acetylene and, in some experiments, carbon monoxide were introduced into the feed stream.

The feed and product compositions were determined on a Khromos GKh-1000 chromatograph equipped with a flame ionization detector and a fused-silica PLOT column (15 m × 0.32 mm, maximum operating temperature of 220°C). The carrier gas was nitrogen. The sampling of the reaction mixture and sample injection were carried out using six-way valves controlled by an SAA-06 analysis automation system. In catalytic tests, while the amount of acetylene was varied, the acetylene conversion was maintained at 30–50%. The changes in the volume of the gas phase during the reaction could be neglected because of the low acetylene concentration in the gas phase. Catalytic activity was measured as the acetylene conversion rate per gram of catalyst (w , (ml C_2H_2) (g Cat) $^{-1}$ min $^{-1}$):

$$w = \frac{X_{\text{C}_2\text{H}_2} V_{\text{C}_2\text{H}_2}}{m_{\text{Cat}}} \quad (1)$$

Here, $X_{\text{C}_2\text{H}_2}$ is the acetylene conversion,

$$X_{\text{C}_2\text{H}_2} = \frac{C_{\text{C}_2\text{H}_2}^0 - C_{\text{C}_2\text{H}_2}^{\text{curr}}}{C_{\text{C}_2\text{H}_2}^0}, \quad (2)$$

where $C_{\text{C}_2\text{H}_2}^0$ is the acetylene concentration in the feed, vol %; $C_{\text{C}_2\text{H}_2}^{\text{curr}}$ is the acetylene concentration in the mixture leaving the reactor, vol %; $V_{\text{C}_2\text{H}_2}$ is the acetylene feed rate, ml/min; and m_{Cat} is the catalyst weight, g.

The ethylene selectivity of the catalyst was determined as the ratio of the amount of ethylene to the amount of reacted acetylene:

$$S_{\text{C}_2\text{H}_4} = \frac{C_{\text{C}_2\text{H}_4}}{C_{\text{C}_2\text{H}_2}^0 - C_{\text{C}_2\text{H}_2}^{\text{curr}}}, \quad (3)$$

where $C_{\text{C}_2\text{H}_4}$ is the ethylene concentration in the mixture leaving the reactor, vol %.

The ethane selectivity of the catalyst was determined using a similar formula:

$$S_{\text{C}_2\text{H}_6} = \frac{C_{\text{C}_2\text{H}_6}}{C_{\text{C}_2\text{H}_2}^0 - C_{\text{C}_2\text{H}_2}^{\text{curr}}}, \quad (4)$$

where $C_{\text{C}_2\text{H}_6}$ is the ethane concentration in the mixture leaving the reactor, vol %.

The contribution from the oligomerization products was estimated as

$$S_{\text{C}_2\text{H}_6} = 1 - S_{\text{C}_2\text{H}_4} - S_{\text{C}_2\text{H}_6}. \quad (5)$$

In order to evaluate the effect of the dilution of the gas phase by the solvent vapor on the chromatographic analyses of the mixture leaving the reactor, we performed “blank” experiments using methane as the mark. In these experiments, a reaction mixture in which helium was replaced with the equivalent amount of methane was fed into the *N*-methylpyrrolidone-containing reactor preheated to 90°C. It turned out that the methane peak areas in the chromatograms of the feed and the mixture leaving the reactor are nearly equal. This might be due to the fact that the outlet pipes of the shaker reactor were cooled by the air, which caused solvent vapor condensation, and the condensate flew back into the reactor. Thus, the diluting effect of the solvent on the mixture leaving the reactor could be neglected in the calculation of reaction parameters.

The identification of the oligomers resulting from the reaction (C₄ and higher) was carried out by the GC-MS method (Agilent Technologies GC-MS 6890N-5973 system, HP-5 MS capillary column).

Identification of the oligomers in the gas phase. The gas mixture leaving the reactor was directed to a trap placed in a Dewar flask containing an acetone–liquid nitrogen mixture, whose temperature was about –70°C. At this temperature, the hydrocarbons of the mixture leaving the reactor (except acetylene, ethylene, and ethane) and the solvent vapor froze on the trap walls. The hydrocarbons were collected in the trap for 5 h. Next, a gas burette filled with water was connected to the trap and the trap was held at room temperature for 15 min. The hydrocarbons condensed in the trap passed into the gaseous state and displaced water from the burette. After the volume of the gas

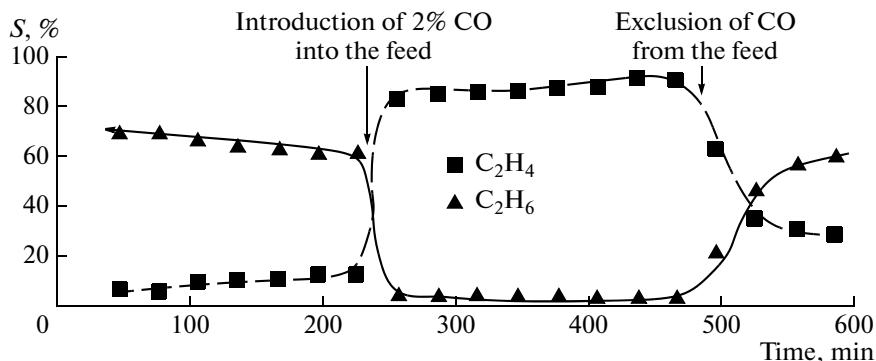


Fig. 1. Change in the C_2H_2 hydrogenation selectivity upon the introduction of 2% CO into the feed and upon the exclusion of the CO from the feed. Reaction conditions: 2% C_2H_2 , 90% H_2 , 8% He, 90°C, *N*-methylpyrrolidone.

phase stopped changing, the burette was disconnected from the trap and the gas was sampled with a syringe to determine its composition by GC-MS.

Identification of the oligomers in the liquid phase. After the run, the liquid phase was separated from the catalyst by filtration or centrifugation, and the filtrate (centrifugate) was sampled with a syringe (sample size of 5 μ l). The sample was analyzed by GC-MS.

RESULTS AND DISCUSSION

Acetylene hydrogenation on the Pd/Sibunit catalyst in the absence of carbon monoxide is low-selective with respect to ethylene. For example, at a low C_2H_2 concentration of 2% and a high hydrogen concentration of 90%, the ethylene selectivity is $S_{C_2H_4} = 11.0\%$. The major reaction product is ethane ($S_{C_2H_6} = 64.6\%$). In addition, acetylene hydroooligomerization products are observed in the reaction mixture (their composition is discussed below). The proportion of acetylene converted into these products is 24.4%. The introduction of CO into the feed stream causes a dramatic change in the proportions of reaction products (Fig. 1), and acetylene hydrogenation to ethylene becomes the dominant route of the reaction over the Pd/Sibunit catalyst.

Three replicas of this experiment were done, and it was established that the addition of CO raises $S_{C_2H_4}$ by a factor of ~ 8 , bringing it to $89.6 \pm 1.5\%$. The ethane formation reaction is strongly hampered, so that the ethane selectivity falls to $S_{C_2H_6} = 1.9 \pm 0.6\%$ and the ethane concentration in the gas phase decreases by a factor of 34. The amount of acetylene converted into hydroooligomers ($8.4 \pm 1.6\%$) decreases by a smaller factor of ~ 3 . Note that the high ethylene selectivity ($89.6 \pm 1.5\%$) persists at a high acetylene conversion of $95.8 \pm 1.3\%$.

The effect of carbon monoxide is reversible in part (Fig. 1). The exclusion of CO from the feed causes opposite changes in $S_{C_2H_4}$ and $S_{C_2H_6}$, specifically, a decrease in the ethylene selectivity and an increase in

the ethane selectivity. However, the reverse process takes place less rapidly: the ethylene selectivity falls from 91 to 30% over 2 h and then remains almost invariable. There is no complete reversibility here since, as was demonstrated above, $S_{C_2H_4}$ in the absence of CO is 11.0%.

Both CO and C_2H_2 are strongly adsorbed by palladium and can compete for active sites of the catalyst [11]. For carbon monoxide, there are at least three forms of adsorption on the palladium surface: multipoint (strongest) adsorption, bridging adsorption, and linear adsorption on a single palladium atom ("monoform"). Cider and Schoon [11] hypothesized that strongly adsorbed CO can remain on the surface even at a high acetylene concentration, changing the electronic state of palladium. As a consequence, after carbon monoxide is excluded from the feed, the decline of ethylene selectivity from 91 to 30% lasts longer (2 h) than the increase in ethylene selectivity from 11 to 90% upon the introduction of CO into the feed stream (40 min).

The above results indicate that, of the two by-product formation routes reducing the ethylene selectivity—ethylene hydrogenation and acetylene hydroooligomerization—the former is more sensitive to the presence of CO than the latter. This is due to the fact that acetylene and ethylene have different capacities for competing with carbon monoxide for active sites of the catalyst. Ethylene is bound to surface palladium atoms much less strongly than acetylene. According to the literature, the ratio of the acetylene and ethylene sorption constants for Al_2O_3 -supported palladium is ~ 2200 at 25°C [12]. The heat of adsorption of C_2H_2 on Pd(100) is 112 kJ/mol [13]. A considerably smaller value of 76 kJ/mol was obtained for ethylene adsorption on Pd(111). The data reported for the heat of adsorption of carbon monoxide are more abundant. The average ΔH_{ads} values for CO on Pd/ SiO_2 , without the existence of different CO adsorption species taken into account, are 92.2–119.8 kJ/mol, depending on the surface coverage and pretreatment conditions [13–17]. Vattuone et al. [13] distinguished the follow-

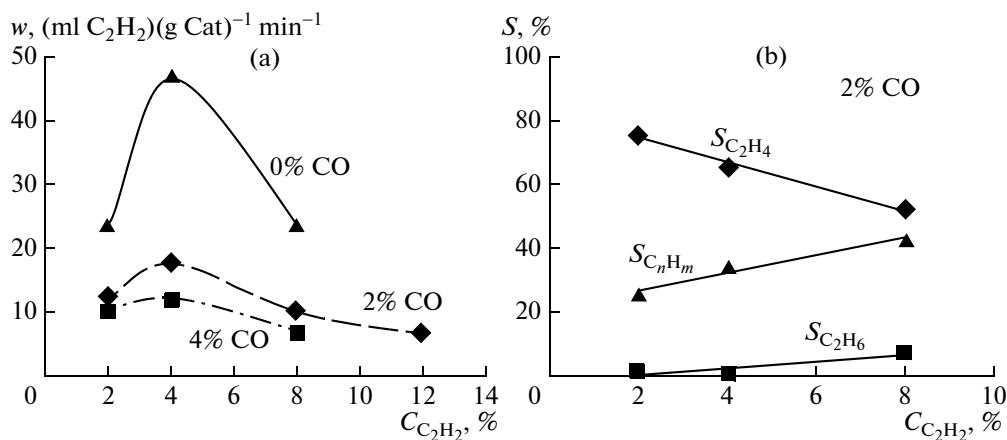


Fig. 2. Effect of the acetylene concentration on the (a) reaction rate and (b) selectivity. Reaction conditions: 90% H_2 , 10% ($C_2H_2 + CO + He$), 90°C, *N*-methylpyrrolidone.

ing three CO adsorption species on Pd(111): multi-bonded CO, $\Delta H_{ads} \approx 196.5$ kJ/mol; bridging CO, $\Delta H_{ads} < 175.6$ kJ/mol; and linearly adsorbed CO, $\Delta H_{ads} < 92.0$ kJ/mol. Dropsch and Baerns [14] reported the values of 167.6 and 75.4 kJ/mol for bridging CO and 50.3–92.2 kJ/mol for linearly adsorbed CO for low and high CO coverages of the surface, respectively. Clearly, both acetylene and carbon monoxide are strongly adsorbed by surface palladium atoms. Some of the carbon monoxide species (multi-bonded and bridging CO) are much more strongly bound to palladium than acetylene. It was demonstrated that, when present in excess, C_2H_2 displaces CO from the Pd/ Al_2O_3 surface [11]. It can be assumed that, under the liquid-phase hydrogenation conditions, acetylene can compete with CO for active sites of the catalyst owing to its high solubility in *N*-methylpyrrolidone—the maximum acetylene concentration in the liquid phase is approximately 150 times higher than its concentration in the gas phase. Acetylene is much more soluble in organic solvents than carbon monoxide. The solubility of C_2H_2 in *N*-methylpyrrolidone at $P = 1$ atm and $T = 20^\circ C$ is $38.7\text{ cm}^3/\text{cm}^3$, and the solubility of CO in the same solvent is $0.055\text{ cm}^3/\text{cm}^3$ [18]. Accordingly, as is demonstrated in this work, acetylene hydrogenation into ethylene takes place even at high CO concentrations in the gas phase (20%), but at a low rate.

The rate-limiting step of ethylene hydrogenation in the presence of CO is conventionally considered to be carbon monoxide desorption from the palladium surface. It is believed that the heat of desorption of CO is a component of the activation energy of this reaction. It was demonstrated that E_a of ethylene hydrogenation on Pd/ SiO_2 in the presence of CO is as large as 112.7 kJ/mol, while the activation energy in the absence of CO is 33.9 kJ/mol [14]. This large increase in E_a (~75.4 kJ/mol) leads to a large decrease in the rate of ethylene hydrogenation in the presence of CO

(the rate constant decreases by approximately 10 orders of magnitude under the assumption that the preexponential factor is invariable), while the acetylene hydrogenation rate decreases by a factor of 2–4 in the CO concentration range examined (Fig. 2). This is the cause of the observed large drop in the ethylene selectivity.

In acetylene hydroooligomerization, CO competes with strongly adsorbed acetylene. As a consequence, the effect of CO in this reaction route in the $C_2H_2-H_2-CO$ system is weaker than in ethylene hydrogenation.

Raising the CO concentration in the gas mixture (C_{CO}) does not exert any significant effect on the ethylene and ethane selectivities once these selectivities have changed to the maximum extent upon the introduction of 2% CO into the CO-free feed. This is explained by the fact that, due to the high heat of adsorption of CO on palladium, the CO coverage of the palladium surface is high even at comparatively low CO concentrations. As a consequence, as C_{CO} is further increased, the surface concentration of CO increases only slightly.

The effect of the acetylene concentration was studied at carbon monoxide concentration of 2 and 4%. In both cases, the activity of the catalyst initially passes through a weak maximum and then decreases with an increasing acetylene concentration (Fig. 2a).

According to the literature, the order of acetylene hydrogenation into ethylene with respect to C_2H_2 varies between 0 and –1, depending on the acetylene concentration [8]. The inhibiting effect of acetylene is also observed in the gas-phase hydrogenation at high acetylene concentrations created at elevated pressures. This is due to the fact that acetylene competes with hydrogen for adsorption sites on the palladium surface.

In the liquid-phase reaction, the concentration of acetylene, which is involved in an adsorption equilibrium with palladium, is increased owing to the high solubility of acetylene in *N*-methylpyrrolidone and is about 7 cm³/cm³ under the reaction conditions. This can slow down the reaction. Along with acetylene, carbon monoxide also competes with hydrogen for adsorption sites on the palladium surface, and, accordingly, the reaction rate in the presence of CO is always lower. It can be assumed that the strongly bound CO adsorption species are not displaced by acetylene owing to their heat of adsorption far exceeding the ΔH_{ads} of C₂H₂ (see above). As a consequence, there are fewer active sites available for acetylene and the reaction slows down.

The selectivity of the reaction depends considerably on the acetylene concentration (Fig. 2b). As the acetylene concentration is raised, $S_{\text{C}_2\text{H}_4}$ decreases and $S_{\text{C}_2\text{H}_6}$ increases. According to Borodzinski and Bond [4], there are two types of active sites on the palladium surface: so-called A-sites, on which only acetylene can be hydrogenated, and E-sites, on which the hydrogenation of both acetylene and ethylene can take place. Carbon monoxide primarily blocks E-sites, thus increasing the ethylene selectivity. Acetylene displaces CO from adsorption sites on the palladium surface, thereby shifting the Pd—CO + C₂H₂ ⇌ Pd—C₂H₂ + CO equilibrium to the right. The displacement of CO from E-sites raises the ethane selectivity because the ethylene resulting from acetylene hydrogenation on these sites does not desorb and undergoes further hydrogenation to ethane, while the ethylene forming on A-sites desorbs because of their small size. This is how the increase in the ethane selectivity is explained. This effect is more pronounced at the lower CO concentration (2%) because the equilibrium in the competition between acetylene and carbon monoxide for active sites of the catalysts is more strongly shifted to the right.

Raising the acetylene concentration increases the contribution from acetylene hydroooligomerization. The proportion of acetylene converted into the hydroooligomers can be as large as 40%.

The identification of reaction products by the GC-MS method demonstrated that the composition of the acetylene hydrogenation products depends on whether CO is present in the feed. When the reaction is conducted in the absence of CO, the gaseous products consist largely of C₂ hydrocarbons (87.5%) and contain a considerable amount of butenes (6.3%). In the presence of CO, the total amount of C₂ hydrocarbons is again fairly large (69.1%), acetylene hydroooligomerization is more pronounced, and the proportion of 2-butene is 3 times higher.

According to the GC-MS analyses of the liquid phase, in the absence of CO the liquid product consists largely of ethylcyclohexadiene (39.2%) and contains considerable amounts of benzene and its derivatives

(31.0% altogether). The mechanism of the formation of these compounds is beyond the scope of this study. In addition, *N*-methylpyrrolidone hydrogenation products were detected, namely, *N*-methylacetamide (16.5%) and *N*-methylpropanamide (7.5%).

When the reaction is conducted in the presence of CO, the resulting liquid phase again contains aromatic compounds, namely, benzene, ethylbenzene, and styrene (~27% altogether). Linear and cyclic unsaturated C₈ hydrocarbons are also detected, whereas hydroooligomerization in the absence of CO involves at most three acetylene molecules. Chain propagation in the presence of CO is possible owing to the decrease in the hydrogenation rate because of the decrease in the amount of surface hydrogen, which is replaced by carbon monoxide. Note that no solvent conversion products were detected in the presence of CO.

The effect of the hydrogen concentration on the characteristics of the reactions in the system is illustrated by Fig. 3. The ethane selectivity remains almost invariable over the C_{H₂} = 30–90% range and is about 1%. In the same C_{H₂} range, $S_{\text{C}_2\text{H}_4}$ increases by a factor of about 2 and the proportion of acetylene involved in hydroooligomerization ($S_{\text{C}_n\text{H}_m}$) decreases by a factor of 2.4. At low hydrogen concentrations, the dominant route is acetylene hydroooligomerization, which accounts for 60% of the reacted C₂H₂.

In the hydrogen concentration range of 30–90%, the catalytic activity increases in proportion to C_{H₂} (Fig. 3a). Acetylene hydrogenation to ethylene is known to be first-order with respect to hydrogen [8]. Two reactions—hydrogenation and hydroooligomerization—take place in the system. The overall order of the reaction with respect to hydrogen, calculated from the observed acetylene conversion rate, is also unity. It is, therefore, likely that the hydroooligomerization reaction is zero-order with respect to hydrogen. It is possible that its rate-limiting step is one of the chain propagation steps, e.g., the insertion of an acetylene molecule into the Pd—C bond of the intermediate compound.

The temperature of the reaction medium exerts a significant effect both on the catalytic activity and on the selectivities of the reactions in the C₂H₂—H₂—CO system (Fig. 4).

The Arrhenius apparent activation energy in the 50–80°C range is 22 kJ/mol. This value is close to the E_a of the diffusion of molecules in the liquid phase, which is 19–46 kJ/mol [19]. This fact suggests that the rate-limiting process under our experimental conditions is the diffusion of substrate and product components through the solvent layer adjoining the catalyst particle. Lowering the reaction temperature decreases the ethylene selectivity by a factor of ~2, from 86.1 to 41.8%, in spite of the presence of CO in the gas mixture. Simultaneously, $S_{\text{C}_2\text{H}_6}$ increases by a factor of ~3 and the proportion of acetylene converted into

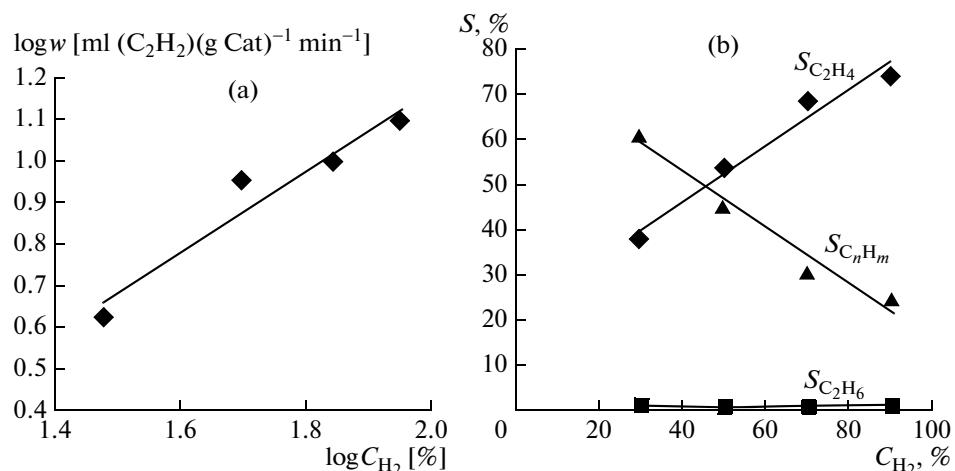


Fig. 3. Effect of the hydrogen concentration on the (a) reaction rate and (b) selectivity. Reaction conditions: 2% C_2H_2 , 2% CO, 94% ($H_2 + He$), 90°C, *N*-methylpyrrolidone.

hydroooligomers increases by a factor of 4.5. This behavior of the system is likely due to the fact that the effective acetylene concentration ($C_{C_2H_2}^{\text{eff}}$) increases as the temperature of the reaction medium is lowered. This increase in $C_{C_2H_2}^{\text{eff}}$ is favored by the following two factors: firstly, a decrease in the reaction temperature causes a decrease in the activity of the catalyst and, accordingly, a decrease in the acetylene conversion; secondly, a decrease in the reaction temperature leads to an increase in the C_2H_2 solubility in *N*-methylpyrrolidone. In the temperature range examined, the C_2H_2 solubility in *N*-methylpyrrolidone increases from ~5 to 15 cm 3 /cm 3 as the temperature is decreased [18]. Both factors favor carbon monoxide replacement by acetylene and an increase in the C_2H_2 :CO ratio on

the catalyst surface, and this causes the observed changes in the reaction characteristics.

These results demonstrate that Borodzinski and Bond's interpretation of the regularities of the gas-phase reactions in the C_2H_2 – H_2 –CO system over the supported palladium catalysts [4], based on the competitive adsorption of CO and acetylene on palladium surface sites, is valid for the liquid-phase processes as well.

Thus, carbon monoxide is an effective palladium modifier for enhancing the selectivity of the catalyst towards acetylene hydrogenation into ethylene in the liquid phase. Carbon monoxide competes with acetylene for active sites of the catalyst. Accordingly, the strongest effect of CO is observed at comparatively low acetylene concentrations in the liquid layer adjoining the catalyst particle.

A low effective acetylene concentration is attained at a low acetylene concentration in the feed and at the highest temperature in the range examined (50–90°C). This temperature ensures the lowest acetylene solubility, the highest acetylene conversion, and, therefore, a low acetylene concentration in the liquid layer adjoining the catalyst particle.

Under the optimum conditions (2% C_2H_2 , 90% H_2 , 2% CO, 90°C), the selectivity of the 0.5% Pd/Sibunit catalyst toward acetylene hydrogenation into ethylene is up to $89.6 \pm 1.5\%$ at a high acetylene conversion of $95.8 \pm 1.3\%$.

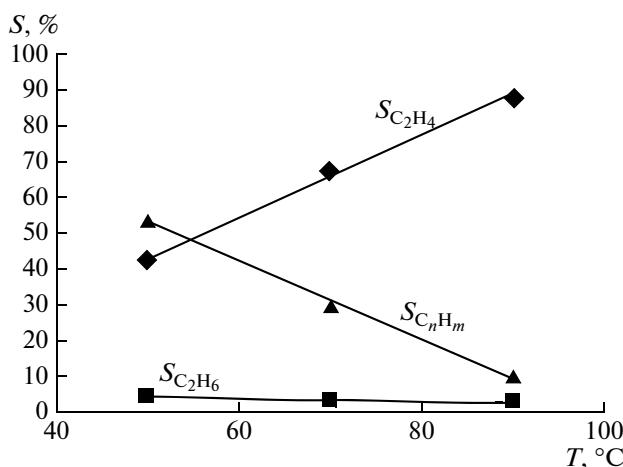


Fig. 4. Temperature effect on the hydrogenation selectivity. Reaction conditions: 2% C_2H_2 , 2% CO, 90% H_2 , 6% He, 90°C, *N*-methylpyrrolidone.

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