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Catalysts Based on Fiberglass Supports:

V. Absorption and Catalytic Properties of Palladium Catalysts Based on a Leached Silica-Fiberglass Support in the Selective Hydrogenation of an Ethylene–Acetylene Mixture

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Abstract—The absorption and catalytic properties of palladium catalysts (0.01% Pd) based on leached soda–silica fiberglass supports were studied in the selective hydrogenation of acetylene as the constituent of an ethylene–acetylene mixture. It was found that fiberglass catalysts exhibited much higher selectivity than traditional supported Pd catalysts. It was suggested that the high selectivity in the reaction of acetylene hydrogenation resulted from the selective absorption (diffusion) of acetylene in the bulk of fiberglass, where Pd microparticles are localized.

INTRODUCTION

Recently, great interest has been expressed by researchers in catalysts based on fiberglass materials [1–8]. It was found that the highly active states of supported components can be formed on fiberglass supports under certain conditions. This can be due to the specific structure of leached glass materials and to the localization of supported metals in them. Thus, it was found [5] that the structure of soda–silica glass fibers can be most adequately described by the model of a pseudolayer intercalation structure that includes alternating layers of several silicon–oxygen tetrahedrons separated by narrow (<4 Å) cavities. Two types of species can be formed upon supporting Pt and Pd on these materials depending on the preparation procedure [7]. Upon standard impregnation, metal particles with a size of several tens of angstrom units were mainly distributed over the outer surface of fibers. These particles are similar in catalytic properties to those supported on traditional carriers (Al_2O_3 and SiO_2) [8]. Upon high-temperature impregnation, the intercalation of Pt or Pd cations into the interlayer spaces of a glass matrix can take place with the formation of localized microparticles (<10 Å) in these spaces. The amount of a metal and the depth of penetration into the bulk of fiberglass can be controlled by the conditions of preparation and by the addition of cointercalates (Cs^+), which are responsible for pillaring effects. In this respect, the structure of fiberglass catalysts is similar to the structure of pillared clays [9, 10]. Note that metal cations and microparticles localized within a glass matrix exhibit a much higher catalytic activity than that of particles distributed over the outer surface of fibers [8].

However, the localization of active centers in the bulk of fiberglass may present transport problems in supplying reactants from a gas phase. It is well known that a glassy state is intermediate between crystalline and liquid states and that glasses can be considered as nonequilibrium supercooled liquids with very high viscosity [11, 12]. As distinct from crystalline substances, glasses do not exhibit fixed phase-transition temperatures. On heating, glasses continuously changed their physicochemical properties (viscosity, conductivity, etc.) and gradually changed from a brittle state to a liquid-drop state. On this basis, it is believed that the solubility and the rate of dissolution (absorption) of gases depend on not only reaction conditions (temperature, concentration, and pressure) but also the properties of gas molecules, such as molecular size, molecular shape, charge, dipole moment, and polarizability. Moreover, the chemical interaction of absorbed molecules with the functional groups of a glass material and with the added active species can play a considerable role. Thus, the apparent rate of reaction depends on not only chemical (catalytic) reaction steps but also the transport (diffusion) of reactants to active centers.

In this work, we attempted to study the effects of the geometric and electrophysical properties of reacting molecules on the activity and selectivity of Pd-containing fiberglass catalysts using the selective hydrogenation of acetylene to ethylene in an ethylene–acetylene mixture. The two reasons for choosing this reaction are given below. First, the molecular sizes of C_2H_2 and C_2H_4 are similar, whereas the electrophysical properties of these compounds are different. Second, this reaction forms the basis of an industrially important process for the catalytic removal of acetylene from ethylene (for example, for the production of polyethylene). In this case, selectivity is a key parameter; that is, it is desirable to maximally hydrogenate acetylene to ethylene; however, the formation of ethane from both C_2H_2 and C_2H_4 should be prevented.

EXPERIMENTAL

Preparation of catalysts. Leached soda–silica glass cloth (CB, $S_{BET} = 1.2$ m^2/g) was impregnated with a $[Pd(NH_3)_4]Cl_2$ solution at ~100°C. Next, it was separated from the impregnating solution, washed with deionized water for the removal of metal compounds weakly bound to the support, dried at 110°C, calcined in air at 300°C for 2 h, and reduced in hydrogen at 300°C for 2 h [5]. The samples prepared by this method, which are denoted 1-CB-0.01Pd and 2-CB-0.01Pd, contained ~0.01 wt % Pd. Samples 1-CB-0.01Pd/Cs and 2-CB-0.01Pd/Cs were prepared in a similar manner; however, Cs^+ cations in an amount of 0.2 wt % were preintercalated into the support. Samples 2-CB-0.01Pd and 2-CB-0.01Pd/Cs were prepared in the same manner as samples 1-CB-0.01Pd and 1-CB-0.01Pd/Cs for the purpose of reproduction. According to the data obtained using XPS in combination with layer-by-layer etching by 2-keV Ar^+ ions at a current of 10 μA [7], in all of the above samples, palladium was completely incorporated in the bulk of fiberglass at a depth of 200–300 Å, whereas metal particles were absent from the outer surface of fibers. The conditions of support preparation and Pd introduction, as well as the distribution of Pd in the bulk of fiberglass, were described previously in more detail [5, 7].

Catalysts containing palladium particles on the outer surface of the support were used as reference samples in the catalytic tests. Leached Na–Si glass cloth and silica gel with a specific surface area of 10 m^2/g and a pore radius of ~1000 Å were used for preparing the reference samples. The active component was introduced by impregnation with a $[Pd(NH_3)_4]Cl_2$ solution at room temperature without the removal of palladium compounds weakly bound to the surface. As found previously [7], in this preparation method, all palladium was supported on the outer surface of fiberglass to form metal particles of size 40–100 Å. The sample thus prepared, which was denoted 5-CB-0.2Pd, contained 0.2 wt % palladium; this concentration is higher than that in the samples prepared by impregnation at elevated temperature by an order of magnitude. The other reference sample, SiO_2–0.25Pd, was prepared by the impregnation of silica gel with a $[Pd(NH_3)_4]Cl_2$ solution, and it contained 0.25 wt % Pd.

Catalytic tests. The prepared catalyst samples were tested in the reaction of selective C_2H_2 hydrogenation to C_2H_4 in an ethylene–acetylene mixture. The tests were performed in a batch-flow reactor under the following conditions: reaction temperatures, 20, 100, and 155°C; reaction mixture composition, $CH_4/C_2H_2/C_2H_4/H_2/Ar = 0.2 : 1.0 : 1.5 : 3.5 : 11$; total pressure of the mixture, 590 torr; circulation rate, 50 ml/s; and catalyst weight, 0.3–2.5 g. Methane served as an internal standard in the chromatographic analysis of mixtures. Hydrogen was taken in an amount required for the complete hydrogenation of acetylene and ethylene to ethane. The catalyst was pretreated in hydrogen ($P = 200$ torr) at 300°C for 1 h. The concentrations of reactants and products in time were measured by chromatography, and the activity of catalysts and selectivity for acetylene were determined from these data. The catalyst activity in acetylene hydrogenation referenced to a unit weight of palladium ($A_{C_2H_2}$) was calculated as the total amount of C_2H_2 reacted in a time of 50% acetylene conversion. The selectivity for acetylene was also calculated from the integrated amounts of acetylene reacted (ΔC_2H_2) and ethane formed (ΔC_2H_6) in a time of 50% conversion of C_2H_2 using the equation $S = \Delta C_2H_2/(\Delta C_2H_2 + \Delta C_2H_6)$.

Studies by temperature-programmed desorption and oxidation. The experiments were performed in a flow reactor at a heating rate of 10 K/min, which was controlled using a PIT-3A isodromic temperature regulator with a 3TA-3 linear voltage controller. The studies were performed with samples 1-CB-0.01Pd and 1-CB-0.01Pd/Sc tested in the selective hydrogenation reaction at 155°C. The sample weight was 0.5–1.0 g, and the gas flow rate was 2 ml/s. In the modes of temperature-programmed desorption (TPD) and temperature-programmed oxidation (TPO), heating was performed in a helium flow and in a mixture of O_2 + He with an oxygen content of 0.3%, respectively. Before thermal desorption, the samples were blown with the corresponding gas mixture at room temperature for 10 min; then, they were heated to 350–500°C and held at the final temperature for 5–10 min. The continuous analysis of a gas phase was performed using a VG Sensorlab 200D quadrupole mass spectrometer with the simultaneous detection of 10 peaks and computer-aided data processing. The concentrations of H_2, H_2O, C_2H_2, C_2H_4, CO, O_2, and CO_2 were determined from the intensities of peaks with $m/e = 2$, 18, 25, 27, 28 (minus the contribution of CO_2), 32, and 44, respectively. The relative sensitivity factors for various components were determined from the analysis of corresponding calibration mixtures prepared with the use of helium as the diluent gas.

IR- and UV-spectroscopic studies. Samples 1-CB-0.01Pd and 2-CB-0.01Pd (both fresh and tested in the hydrogenation of an ethylene–acetylene mixture) were preevacuated at a temperature of 200°C and a pressure of 10^{-2} torr for 30 min. The IR spectra were measured in air on a Shimadzu 8300 Fourier spectrometer equipped with a DRS-8000 attachment using the diffuse-reflectance technique. The spectra were recorded with a resolution of 4 cm^{-1}, and the number of scans was 50. The procedures of glass-cloth sample preparation and IR-spectroscopic measurements were described in detail elsewhere [5]. The IR spectrum of gaseous acetylene was measured at an acetylene pressure of 10 torr with the use of a standard cell with a length of 10 cm. The UV spectra of the tested samples without pretreatment were measured on a Shimadzu 4501 spectrometer equipped with an ISR-240A diffuse-reflectance attachment over a range of 190–900 nm with a resolution of 4 nm.

RESULTS

Catalytic Properties of Fiberglass Catalysts in the Selective Hydrogenation of an Ethylene–Acetylene Mixture

Table 1 indicates that only the reference samples in which Pd particles were localized on the outer surface were active in the reaction of acetylene hydrogenation at room temperature. At the same time, catalysts containing Pd only in the bulk of fiberglass (samples 1-CB-0.01Pd and 2-CB-0.01Pd) did not exhibit any detectable activity in the hydrogenation of acetylene or ethylene under these conditions. Similar behavior was observed at 100°C. The activity of these samples dramatically increased only as the reaction temperature was increased up to 155°C. In this case, the reaction selectivity was close to 100%; that is, only acetylene was hydrogenated in the presence of ethylene (Table 1). This fact is unusual, because, as a rule, selectivity decreases with temperature. Note that the activity of the catalysts with preintercalated cesium was almost doubled, whereas the selectivity remained almost unchanged.

Considerable differences between catalysts with different palladium localization can also be found by comparing the time dependence of the composition of reaction mixtures (Fig. 1). In the case of reference samples, in which palladium occurred on the outer surface of fiberglass or in the pores of silica gel, acetylene was mainly hydrogenated to ethylene at an initial period (Figs. 1a, 1b). However, as the concentration of acetylene in the mixture decreased, the concentration of ethane dramatically increased because of an increase in the rate of ethylene hydrogenation to ethane. This behavior is typical of palladium catalysts on traditional supports (Al_2O_3 and SiO_2) and can be explained by the fact that acetylene at high concentrations blocks the surface of palladium and hence prevents the nonselective hydrogenation of ethylene [13, 14]. As the fraction of C_2H_2 in the mixture decreased, the surface of Pd became free of acetylene to dramatically increase the rate of C_2H_4 hydrogenation.

The glass-cloth catalysts with palladium particles in the bulk of fiberglass exhibited a distinctly different character of the time dependence. As can be seen in Fig. 1c, the reaction of ethylene hydrogenation to ethane did not occur even after almost complete conversion of acetylene. This result seems very surprising, taking into account unusually high temperatures for selective hydrogenation and the presence of large amounts of ethylene and hydrogen. Nevertheless, it can be easily explained if we assume that C_2H_2 and H_2 rather than C_2H_4 molecules penetrate (diffuse) into the bulk of a glass matrix. In other words, Pd particles are inaccessible to ethylene; consequently, almost 100% selectivity of acetylene conversion was observed. It is likely that the problem of reactant transport to active centers is responsible for the fact that acetylene was not hydrogenated at low temperatures.

TPD and TPO Studies

When TPD in a helium flow was performed in sample 1-CB-0.01Pd that was tested in the reaction, the desorption of water was observed as two broad peaks: a clearly defined peak at 100–200°C and a very weak peak at ~350°C (Fig. 2a, curve *1*). The shape of the TPD curve indicates that this sample contained a large amount of weakly bound water that resulted from contact with air. The desorption of water began almost at room temperature; at 75–80°C, the concentration of water reached a plateau, and the rate of desorption remained constant in the course of a further increase in

Table 1. Activities ($A_{C_2H_2}$) and selectivities ($S_{C_2H_2}$) of various Pd–glass cloth catalysts and reference samples in the reaction of selective acetylene hydrogenation

Sample	Pd and Cs contents, wt %	$A_{C_2H_2}$, mol (g Pd)$^{-1}$ min^{-1}	$S_{C_2H_2}$, %
1-CB-0.01Pd	0.01	0.131	99
2-CB-0.01Pd	0.01	0.076	95
1-CB-0.01Pd/Cs	0.01 Pd + 0.2 Cs	0.272	94
2-CB-0.01Pd/Cs	0.01 Pd + 0.2 Cs	0.235	98.5
Reference samples			
5-CB-0.2Pd	0.20	0.014	83
SiO_2-0.25Pd	0.25	0.023	89

Note: The reaction temperature was 155°C in entries 1–4 or 20°C in entries 5, 6.

the temperature. Such a behavior when the rate of desorption is independent of temperature is typical of processes where the rate is controlled by mass transfer. It is likely that a fixed amount of water is removed from the bulk of the glass matrix, and the rate of this removal is limited by the transfer through a glass–gas interface. As the temperature was increased up to 220–230°C, desorption was abruptly terminated because of the complete disappearance of weakly bound water. The total amount of liberated H_2O was 5.5×10^{20} molecule/g or ~2% of catalyst weight. At higher temperatures, acetylene and CO_2 (the amount of CO was no higher than 15% of CO_2) were released into the gas phase, and the total amount of these compounds was lower than the amount of liberated water by approximately two orders of magnitude. Note that ethylene and hydrogen were not observed in the TPD curves.

Another TPD curve was observed in sample 1-CB-0.01Pd/Cs with preintercalated Cs^+ (Fig. 2b, curve *1*). The desorption of weakly bound water species exhibited a pronounced maximum at 100°C, and it did not reach a plateau. Moreover, the weakly pronounced second peak of water release was much more clearly defined, and it exhibited a maximum at 300°C. In this case, the total water content increased by a factor of ~1.5. Thus, the modification of fiberglass with cesium cations increased its absorption capacity for water. The change in the shape of a thermal-desorption curve and the increase in the absorption capacity indicate that the introduction of Cs^+ considerably changed the system of internal cavities and channels toward an increase in the interlayer spacing. The effect of Cs^+ on the properties of leached glass cloth is analogous to a well-known pillaring effect in layer structures: a change in the size of interlayer cavities upon introducing cations, anions, or neutral molecules into them [9, 10]. The possibility of this effect was found previously [5] in a study of the state of Cs^+ introduced into the bulk of leached fiberglass by ^{133}Cs NMR spectroscopy. This effect can partially remove diffusion limitations on the penetration of reactants to active centers; it is likely that this fact can explain an increase in the activity of Cs-containing samples (Table 1). Nevertheless, an increase in the second peak of water desorption and the tailing of the first thermal-desorption peak suggest that additional structures that bind water in the bulk of fiberglass can be formed in the presence of Cs. This is most likely due to the well-known ability of the cesium cation to solvate water molecules (hydroxyls). Thus, it is believed that the introduction of cesium increases the rate of reactant diffusion; however, diffusion limitations on water remained, although their character was somewhat different from those in the case of cesium-free samples.

Samples 1-CB-0.01Pd and 1-CB-0.01Pd/Cs tested in the selective hydrogenation reaction were also examined by TPO in an oxygen-containing mixture. In this case, the shapes of TPO and TPD curves were almost identical with respect to weakly bound water (cf. curves *1* and *2* in Fig. 2a), as can easily be seen in the difference

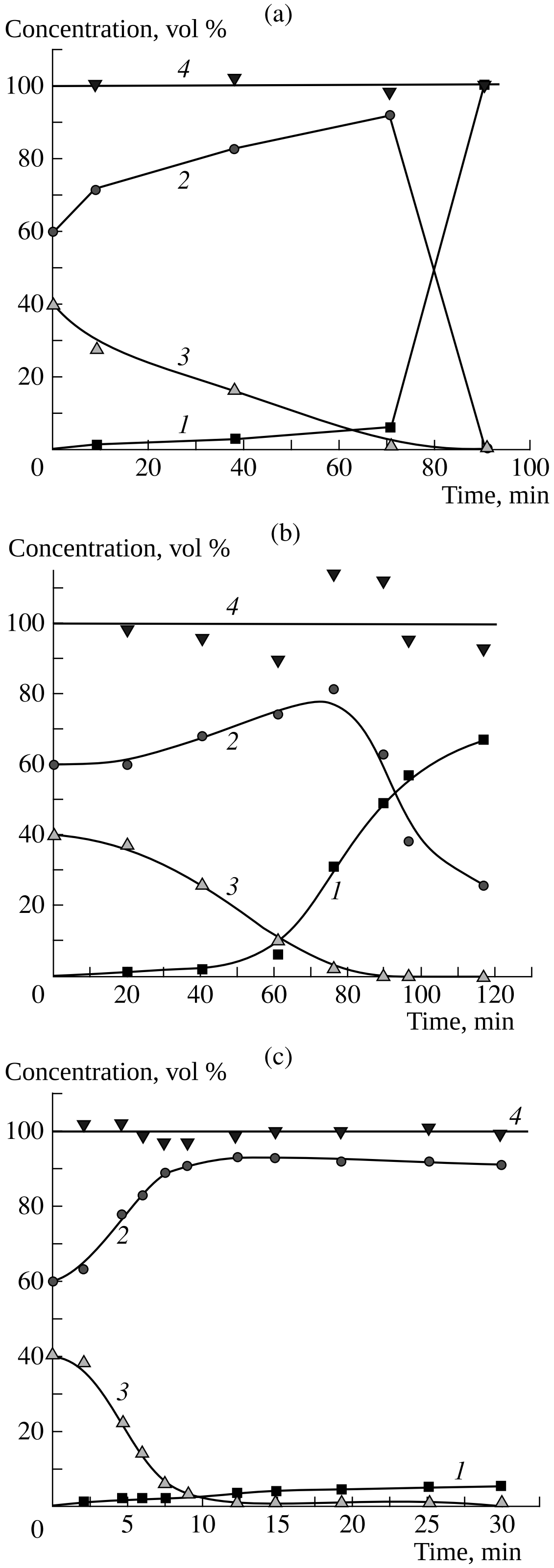

Fig. 1. The time dependence of the concentrations of (*1*) C_2H_6, (*2*) C_2H_4, and (*3*) C_2H_2 and (*4*) the total concentration ($\Sigma(C_2H_x)$) in the selective hydrogenation reaction of an ethylene–acetylene mixture on the following catalysts: (a) SiO_2-0.25Pd (20°C), (b) 5-CB-0.2Pd (20°C), and (c) 1-CB-0.01Pd (155°C).

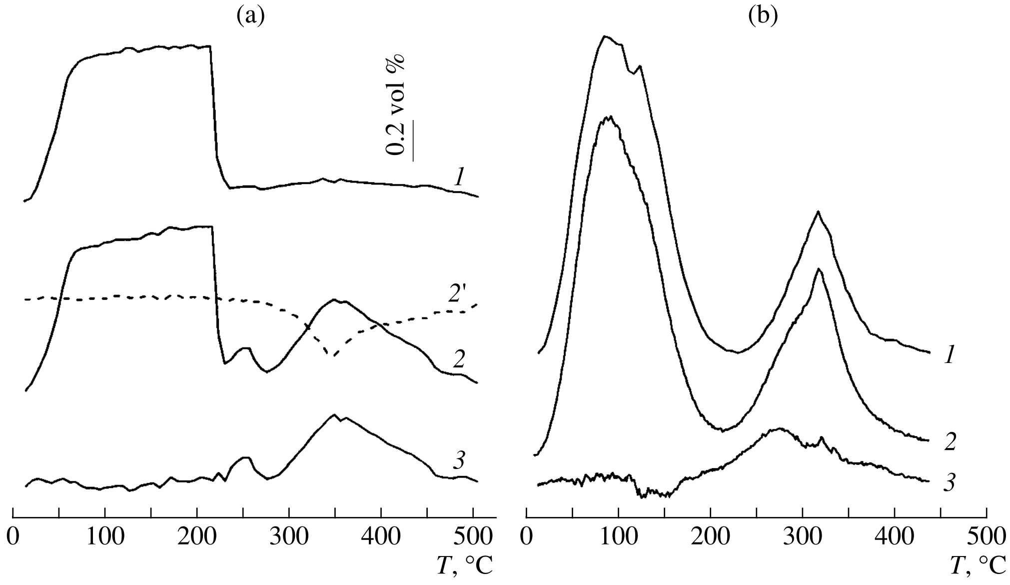

Fig. 2. Curves of the temperature-programmed (*1*, *2*) desorption of water and (*2'*) absorption of oxygen measured in a flow of (*1*) helium or (*2, 2'*) a mixture of 0.3%O_2 + He in samples (a) 1-CB-0.01Pd (155°C) and (b) 1-CB-0.01Pd/Cs (155°C) and (*3*) the difference spectrum (*2*–*1*).

spectrum (curve *3*). The appearance of a pronounced peak of water with a maximum at 350°C accompanied by the absorption of oxygen (dashed line) has engaged our attention. The amount of formed CO_2 was higher than the total amount of acetylene and CO_2 released upon TPD in helium by a factor of ~4 (on a carbon-atom basis). In this case, approximately 0.8×10^{20} molecule/g oxygen was absorbed, and about 0.2×10^{20} molecule/g carbon dioxide was released (not shown in Fig. 2a), that is, several times lower than the amount that corresponds to the stoichiometry of the deep oxidation of acetylene: $2C_2H_2 + 5O_2 \longrightarrow 4CO_2 + 2H_2O$. At the same time, in contrast, the amount of released water (1.5×10^{20} molecule/g) estimated from the difference spectrum was much higher, and it is close to the stoichiometric value for the hydrogen oxidation reaction $2H_2 + O_2 \longrightarrow 2H_2O$. Note that the number of H_2 molecules extracted from the catalyst as H_2O is higher than the number of Pd atoms by a factor of ~200; that is, this hydrogen cannot be chemically bound to palladium. Taking into account this fact and the absence of H_2 and C_2H_4 molecules absorbed in the course of the reaction, we can assume that acetylene or, more precisely, its oligomers, which are readily formed under reaction conditions, especially at elevated temperatures, serve as a source of hydrogen. Indeed, the formation of acetylene oligomers in the course of the hydrogenation reaction of an ethylene–acetylene mixture was found in a number of studies [13–16]. Sarcany *et al.* [14] noted the presence of labile hydrogen in the oligomers and the participation of this hydrogen in a hydrogenation reaction. Thus, a comparison between the total amounts of released CO_2 and H_2O indicates that a considerable portion of carbon-containing compounds was firmly retained in the bulk of a glass matrix rather than burned up to 500°C. In the TPO of sample 1-CB-0.01Pd/Cs containing cesium, the intensity of the second peak of water also increased (Fig. 2b, curve *2*). The additional amount of released water calculated from the difference spectrum was close to an estimated value for sample 1-CB-0.01Pd.

Results of UV- and IR-Spectroscopic Studies

Figure 3 demonstrates the UV spectrum of sample 2-CB-0.01Pd that was tested in the reaction of selective acetylene hydrogenation. The spectrum exhibits broad absorption bands at 25900 and 40000 cm^{-1}, which can be attributed to polyene structures containing six and three conjugated double bonds, respectively [17]. This provides support to the hypothesis that acetylene oligomerization occurred in the course of selective acetylene hydrogenation on glass-cloth catalysts with the formation of extensive and tightly bound structures. We believe that these structures are linear rather than cyclic. Indeed, a cyclic compound with three conjugated double bonds is benzene, which is characterized by an absorption band at 38500 cm^{-1} split into several narrow components; this band was not observed experimentally. A cyclic compound with six conjugated double bonds is thermodynamically unstable, and it will decompose with the formation of two benzene molecules. At the same time, the pseudolayer structure of a glass matrix is favorable for the formation and stabilization of linear rather than cyclic structures.

The IR spectra of samples 1-CB-0.01Pd and 2-CB-0.01Pd that were tested in the selective hydrogenation reaction (Fig. 4, curves *1*, *2*) exhibited absorption bands at

3235, 3290, and 3320 cm^{-1} in the range 3100–3450 cm^{-1}. This range is typical of the C–H stretching vibrations of acetylene hydrocarbons [18]. Indeed, in the region 2000–2200 cm^{-1}, a weak band at 2070 cm^{-1} was detected, which can be attributed to the vibrations of the triple bond C≡C. Moreover, the IR spectra exhibited a narrow band at 1610 cm^{-1} (Fig. 4), which can be due to the occurrence of compounds containing conjugated double bonds in the bulk of fiberglass.

A comparison of the IR spectra of the samples with the spectrum of acetylene in a gas phase (Fig. 4, curve *3*) allowed us to conclude that acetylene was present in the bulk of fiberglass. Indeed, if a set of narrow rotational components characteristic of the IR spectra of gaseous substances is neglected, the similarity of the contours of curves *1–3* is evident. Nevertheless, acetylene that occurs in the bulk of fiberglass is different from acetylene molecules in a gas phase or in the pores of ordinary porous materials. First, as distinct from gaseous acetylene, the IR spectrum of absorbed acethylene (in the range 3100–3450 cm^{-1}) is considerably broadened. Second, the band at 2070 cm^{-1} due to the stretching vibrations of the triple bond is shifted to a high-frequency region from a position at 1973 cm^{-1}, which is characteristic of acetylene in a gas phase. Similar regularities were observed in the studies of benzene adsorption on zeolites [19, 20]. In these studies, a shift of the characteristic bands of benzene in a region of 1800–2000 cm^{-1} to a high-frequency region was observed, as compared with liquid benzene, and this shift increased with decreasing pore size of zeolites. This behavior was explained by the interaction of the benzene ring with zeolite pore walls. We believe that in our case the spectrum of absorbed acetylene was also changed because of weak interactions between acetylene and the functional groups of a glass matrix, most likely, with hydroxyls.

Thus, UV- and IR-spectroscopic data indicate the presence of acetylene and its oligomerization products in the samples tested in the selective hydrogenation reaction.

DISCUSSION

Based on previously published data [5, 7], we believe that the penetration of various molecules into the bulk of leached glass cloth depends on both the temperature and the properties of the molecules.

Thus, according to ^{129}Xe NMR data, spherically symmetrical Xe atoms did not diffuse into the bulk of fiberglass even at a temperature of 300°C. At the same time, charged particles (cations) or easily polarizable molecules were readily sorbed even at room temperature. We also discovered the ability of fiberglass to sorb cations such as Na^+, Cs^+, Pt^{2+}, and Pd^{2+} from solutions. Recently, we obtained experimental data on the high low-temperature sorption of NO, which are also indicative of the effective diffusion of these polar molecules to active centers localized in the bulk of fiberglass. It is likely that diffusion problems were responsible for the absence of activity in the deep oxidation of such nonpolar molecules as propane and butane at low temperatures (< 250°C) [8]. High activity was observed only at much higher temperatures when the electrophysical properties of molecules have an insignificant effect on their transport to active centers. A similar behavior was also observed in the reaction of selective acetylene hydrogenation, which was studied in this work. Indeed, fiberglass catalysts were active only at 155°C, whereas they were altogether inactive in the temperature region 20–100°C.

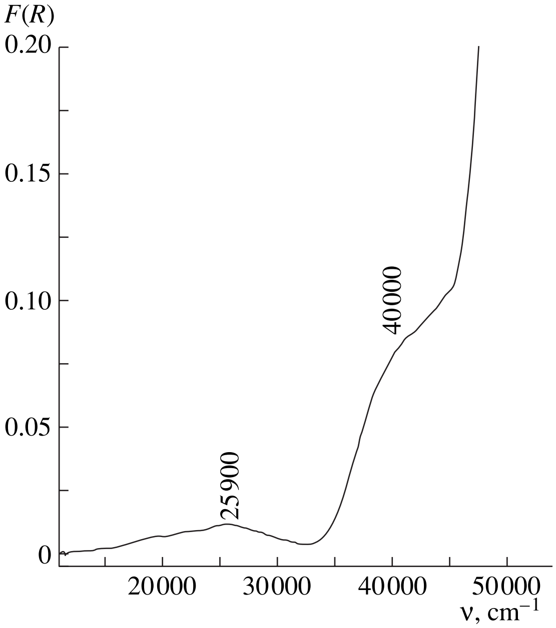

Fig. 3. UV spectrum of sample 2-CB-0.01Pd after testing in the selective hydrogenation reaction at T = 155°C.

Based on the above data, it is believed that, at least in the region of low temperatures, the electrophysical properties (charge, dipole moment, and polarizability) of various molecules are of considerable importance in their transport into the bulk of fiberglass.

In the case of C_2H_2 and C_2H_4 molecules, the ability to diffuse into fiberglass can depend on differences in their polarizability. Indeed, data given in Table 2 are indicative of a higher ability of acetylene to C–H bond polarization as compared to ethylene and, especially ethane. For example, the higher solubility of acetylene in water, which is higher than the solubility of ethylene by almost one order of magnitude, is a result of this. In this context, the diffusion of reactants into the bulk of fiberglass can be considered as a process analogous to the dissolution of polar molecules in a polar solvent. Consequently, even at a very low concentration of acetylene in a gas phase, its concentration in the bulk of a glass matrix can be high so that ethylene hydrogenation does not take place.

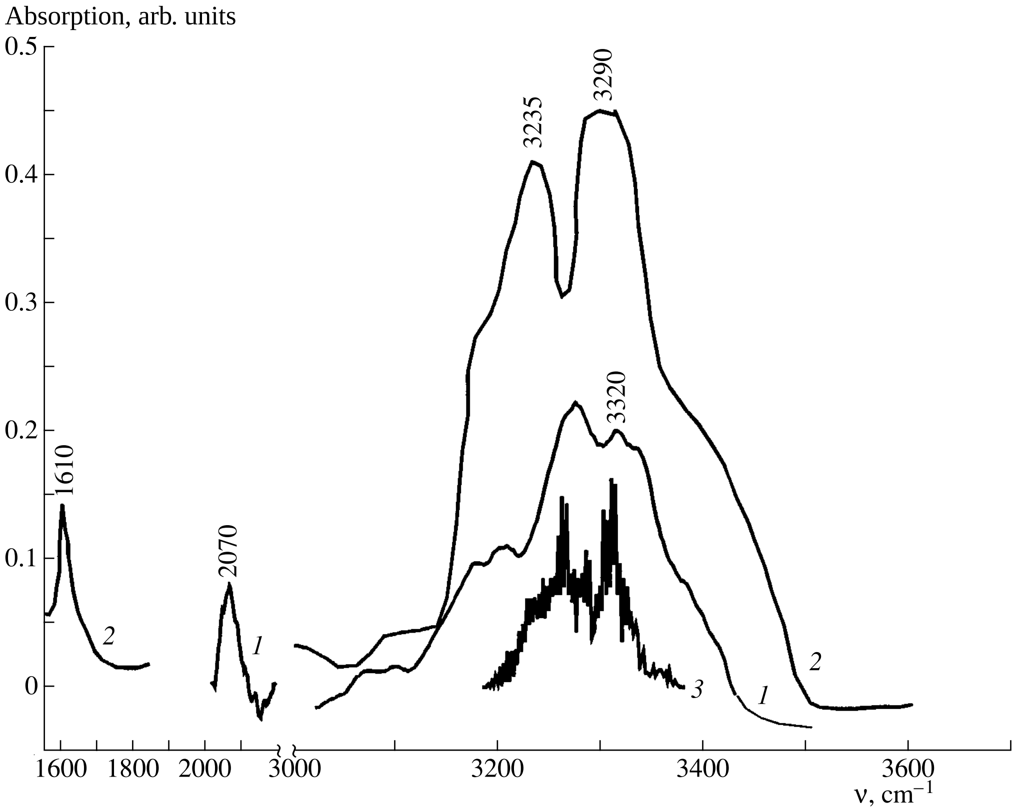

Fig. 4. IR spectra of glass-cloth catalysts after testing in the hydrogenation reaction of a mixture of ethylene and acetylene: (*1*) sample 1-CB-0.01Pd (155°C), (*2*) sample 2-CB-0.01Pd (155°C), and (*3*) the spectrum of acetylene in a gas phase.

UV- and IR-spectroscopic data and the results of thermal-desorption experiments suggest that the catalyst tested in the reaction of selective acetylene hydrogenation contains polyene compounds along with acetylene. It is likely that these compounds contain three and six conjugated double bonds. These compounds can result from the oligomerization of acetylene in the course of reaction. They can be firmly retained in fiberglass microcavities because of steric hindrances or interactions with the functional groups of a glass matrix. On heating in a mixture of $O_2 + He$, these compounds can undergo oxidative dehydrogenation with the formation of allene and polyyne structures and the release of water into a gas phase. For example, this was supported by the darkening of a sample after TPO, as compared with the sample after TPD in a helium flow.

Table 2. Dipole moments of C–H bonds ($\mu_{C\text{–}H}$) [21], energies of the heterolytic dissociation of C–H bonds in a gas phase (ΔG) [22], and water solubilities at 0°C (α) [23] for C_2 hydrocarbons

Hydrocarbon	$\mu_{C\text{–}H}$, debye	ΔG, kJ/mol	α, cm^3/l
C_2H_2	1.0	337.6	1730
C_2H_4	0.6	384.2	226
C_2H_6	0.3	408.6	93.7

In our opinion, the formation of tightly bound hydrogen-deficient structures is responsible for a considerable deviation of the amounts of desorbed CO_2 and H_2O from the reaction stoichiometry of deep acetylene oxidation. Based on the amount of released CO_2, we estimated that palladium fiberglass catalysts could retain up to 0.14 wt % acetylene in the bulk. This amount increased up to 0.5 wt % if the calculation was performed based on the amount of released water, that is, taking into account allene or polyyne structures that remained in the bulk of fiberglass. Therefore, glass-cloth catalysts can selectively sorb acetylene from a gas phase and firmly retain it in considerable amounts.

Thus, we can state that, as distinct from traditional supported catalysts, the catalytic activity of fiberglass catalysts depends on not only the steps of chemical interactions between reactants and active centers but also the transport of the reactants to the bulk of a glass matrix. Molecules that have a higher dipole moment or are easily polarizable will effectively diffuse to active centers to provide the low-temperature activity. At the same time, nonpolar molecules can reach active centers only at elevated temperatures. Thus, the appearance of unusual temperature–concentration relationships can be expected in the kinetic studies of catalytic reactions on fiberglass catalysts with the participation of molecules different in electrophysical properties (for example, the oxidation of polar molecules or deNO$_x$ in the presence of O_2).

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