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Hydrogenation of acetylene–ethylene mixtures on a commercial palladium catalyst

A. Borodziński

Institute of Physical Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-224 Warsaw, Poland
E-mail: Andbor@ichf.edu.pl

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The hydrogenation of acetylene and acetylene–ethylene mixtures on a commercial palladium catalyst for hydrogenation of acetylene traces in ethylene-rich feedstock was studied. The obtained results suggest that during the reaction two types of catalytic sites are created by carbonaceous deposits on the palladium surface: **A** sites representing small spaces and **E** sites representing large spaces of palladium between the carbonaceous deposits. The **A** sites adsorb acetylene and hydrogen but, due to steric hindrance, do not adsorb ethylene. Consequently, these sites are involved in the conversion of acetylene, producing ethylene and small amounts of ethane and butadiene, and they are inactive in the hydrogenation of ethylene. Instead, the **E** sites adsorb all reactants and, therefore, they are responsible for the hydrogenation of ethylene and butadiene at low acetylene partial pressures.

Keywords: hydrogenation of acetylene–ethylene mixtures, palladium catalyst, carbonaceous deposits

1. Introduction

In cracking plants a removal of traces of acetylene from ethylene-rich feedstock is carried out by selective hydrogenation of acetylene on palladium-based catalysts. The unique ability of palladium to the selective hydrogenation raises the question of its origin. However, the mechanism of the complex process, additionally complicated by various transformations undergone by the catalyst in the course of the reaction, is still controversial [1]. During the reaction palladium may convert into β-PdH [2] and/or into PdC_x solution [3–6] and various carbonaceous species, C_xH_y, are deposited on the catalysts [7–26]. The deposits located on the support may increase undesirable hydrogenation of ethylene to ethane by: (i) increase of hydrogen spillover (ethylene hydrogenation on the support) [14,16,17], (ii) increase of intraparticle mass transfer limitation for acetylene and consequently increase of ethylene to acetylene ratio and ethylene hydrogenation in the interior of catalyst particles [18,19]. The effect of carbonaceous deposits located on the metal surface has got various explanations. According to Webb et al. [7–9] hydrogenation of acetylene proceeds in the second layer, i.e., on the top of the irreversibly adsorbed first layer. It was supposed that the C_xH_y species play a role of the hydrogen transfer agent from palladium to acetylene that is adsorbed in the second layer. A similar mechanism has been proposed for hydrogenation of ethylene over palladium [27,28] and platinum [29]. Another explanation of the effect of carbonaceous deposits was presented by Ponec et al. [11–13]. These authors proposed that carbonaceous deposits are in fact inactive, but act only as a selectivity modifier. It was supposed that the deposits diminish abundance of large palladium ensembles that are responsible for the hydrogenation of acetylene to ethane and hardly affect abundance of small palladium ensembles responsible for the hydrogenation of acetylene to ethylene. The reasons of these discrepancies in the works by Webb et al. [7–9] and Ponec et al. [11–13] may be associated with a variety of experimental conditions. This regards particularly the ratio of pressures of acetylene to hydrogen. A different explanation of the role of carbonaceous deposits was offered by Sárkány et al. [30], for the case of hydrogenation of 1,3-butadiene over the $Pd_2Ni_{50}Nb_{48}$ alloy. The authors suggest that carbonaceous deposits more effectively compete on the metal surface with weakly adsorbed n-butane than with strongly adsorbed 1,3-butadiene.

It was shown that experimental conditions during stabilisation of the alumina-supported palladium catalyst, in the course of hydrogenation of acetylene–ethylene mixtures, have an important effect on its final activity and selectivity [20,31]. Larsson et al. [20] have found that the increase of hydrogen coverage during the stabilisation decreases the selectivity to ethane. They assumed that the hydrogen coverage influences the proportion of “harmful coke” to “harmless coke” deposited on the catalyst. The first type of coke was proposed to be responsible for the increase of the selectivity. However, TPO analysis of the coke composition did not confirm the presence of the two types of coke.

Recently, we proposed the mechanism of hydrogenation of acetylene–ethylene mixtures on Pd/α-Al_2O_3, taking into account the role of carbonaceous deposits [22,23]. It was suggested that the deposits formed during the reaction on palladium give rise to three different types of active sites that show specific properties in the hydrogenation of acetylene and ethylene. The mechanism is similar to that proposed recently by Duca et al. [24,25], however our model was used not only to explain activity but also selectivity.

This paper verifies the proposed mechanism [22,23] of the hydrogenation of acetylene and acetylene–ethylene mixtures using commercial catalysts. The kinetic studies carried out at a wide range of acetylene and ethylene pressures in steady-state conditions have shown that the mechanism of the reaction on the commercial catalyst is similar to that reported previously for other Pd/α-Al_2O_3 catalysts [23]. Analysis of experimental results shows that the carbonaceous deposit acts as a modifier of the palladium surface and a transmitter of hydrogen atoms to reacting molecules of acetylene.

2. Experimental

2.1. Materials

The examinations were carried out on the commercial C-31-1A catalyst from CCI (0.038% Pd/α-Al_2O_3), used for the tail-end process of the purification of ethylene feedstock from acetylene.

Ethylene (MZPiR, Poland, 99.96%), argon (99.99%, Plasco), and two preblended mixtures containing 5.0% H_2 in Ar and 0.46% C_2H_2 in Ar (H_2 – AgaGas, 99.999%; C_2H_2 – Matheson, 99.6%; Ar – AgaGas, 99.995%) were used. The $C_2H_2 + \mathrm{Ar}$ mixture was purified when prepared, by removing oxygen, water and acetone. All gases, except $C_2H_2 + \mathrm{Ar}$, were purified in a series of columns packed with Cu/SiO_2, silica gel and molecular sieve 5A.

2.2. Apparatus

The kinetics of hydrogenation of acetylene–ethylene mixtures was measured in a glass flow system equipped with a gradientless microreactor [32]. The inlet stream was obtained by mixing C_2H_4, Ar, and the above-mentioned preblended mixtures. Flow rates and hence compositions of the inlet mixture were set with the aid of mass flow controllers. Composition of both the inlet and outlet streams was measured by GC. Concentrations of ethane, ethylene, and acetylene were determined using a 2 m Carbosieve S column maintained at 403 K and a FID detector. Concentrations of the C_4 hydrocarbons were determined using a 1.5 m EESB/chromosorb P Philips column maintained at 345 K and a FID detector. Concentration of hydrogen was determined using a 6 m molecular sieve 5A column at ambient temperature and a TCD detector. Flow rates, sampling, and data acquisition were computer controlled.

2.3. Experimental procedure

The catalyst used for measurements of both dispersion of palladium and kinetic studies was subject to the following *in situ* pretreatments: (i) calcination in an oxygen stream at 573 K for 0.5 h; (ii) reduction in a hydrogen stream at 573 K for 1 h; (iii) desorption of hydrogen in an argon stream at 723 K for 1 h. Dispersion of palladium, FE (fraction exposed), was determined from the following measurements: (i) chemisorption of oxygen at 293 K; (ii) titration of adsorbed oxygen by hydrogen at 343 K; (iii) titration of chemisorbed hydrogen by oxygen at 293 K. The measurements were performed by a pulse method in a glass system equipped with a TCD cell [33,34]. In the calculation of FE it was assumed that O/Pd_S equals 0.66 [35] and H/Pd_S equals 1.0 [36]. The fraction exposed of the C-31-1A catalyst, determined as an average value from the measurements, was equal to 0.28. The mean diameter of palladium crystallites, d, was calculated from the general equation [37] for FE > 0.2:

$$d = \frac{3.32 d_{\mathrm{at}}}{\mathrm{FE}^{1.23}}, \qquad (1)$$

where d_{at} is the atomic diameter of palladium equal to 2.74 Å. The calculated mean diameter of palladium crystallites was equal to 43.6 Å.

The kinetic studies of hydrogenation of acetylene–ethylene mixtures were carried out for 0.040 g of the catalyst in the form of fine powder (fraction <400 mesh (ASTM)). Before the measurement the catalyst was stabilised under the reaction conditions (inlet gas mixture: 0.16 vol% C_2H_2, 40 vol% C_2H_4, and 0.76 vol% H_2 in Ar; flow rate 20 cm^3/min; 16 h at 351 K and 6 h at 343 K). During the stabilisation both the rate of acetylene hydrogenation and the rate of ethane formation gradually increase, attaining steady states after about 12 h.

The kinetic measurements consist in measuring rate and selectivity of the reaction at a wide range of partial pressure of acetylene, $p_{C_2H_2}$, and ethylene, $p_{C_2H_4}$, over the catalyst. This was attained by varying from run to run partial pressures of these reactants in the inlet stream and the flow rate of the reaction mixture [38]. After each change, steady state of the reaction was attained quickly (less than 15 min), and the sequence in which the changes were executed had no effect on the results. In the presented measurements, the pressure of acetylene over the catalyst varied in the range 0.0035–0.108 kPa, and the pressure of ethylene in the range 0.047–40.0 kPa. The absence of any influence of both external and internal diffusion under operating conditions was adequately checked [39]. Chromatographic analyses of inlet and outlet stream were used to determine the reaction rates: $r_{C_2H_2}$ – rate of acetylene consumption, $r_{C_2H_6}$ – rate of ethane production, and r_{C_4} – rate of C_4 hydrocarbon production. The rate of ethylene production, $r_{C_2H_4}$, was calculated as difference of the rate of ethylene formation from acetylene and the rate of ethylene hydrogenation to ethane, using the following relation:

$$r_{C_2H_4} = \left(r_{C_2H_2} - r^{*}_{C_2H_6} - r^{*}_{C_4}\right) - r^{**}_{C_2H_6}, \qquad (2)$$

in which $r^{*}_{C_2H_6}$ is the rate of ethane formation from acetylene, $r^{*}_{C_4}$ is the rate of acetylene conversion to C_4 hydrocarbon, and $r^{**}_{C_2H_6}$ is the rate of ethane formation from ethylene.

Considering that $r^{*}_{\mathrm{C_2H_6}} + r^{**}_{\mathrm{C_2H_6}} = r_{\mathrm{C_2H_6}}$ and $r^{*}_{\mathrm{C_4}} = 2r_{\mathrm{C_4}}$, the above equation simplifies to the formula

$$r_{\mathrm{C_2H_4}} = r_{\mathrm{C_2H_2}} - r_{\mathrm{C_2H_6}} - 2r_{\mathrm{C_4}}. \tag{3}$$

The overall selectivities of the hydrogenation of acetylene–ethylene mixtures to ethane, ethylene and C_4 hydrocarbons, were calculated as

$$S_{\mathrm{C_2H_6}} = \frac{r_{\mathrm{C_2H_6}}}{r_{\mathrm{C_2H_2}}}, \tag{4}$$

$$S_{\mathrm{C_2H_4}} = \frac{r_{\mathrm{C_2H_4}}}{r_{\mathrm{C_2H_2}}}, \tag{5}$$

$$S_{\mathrm{C_4}} = \frac{2r_{\mathrm{C_4}}}{r_{\mathrm{C_2H_2}}}. \tag{6}$$

A considerable problem in the kinetics of hydrogenation of acetylene–ethylene mixtures measurements was that any change of partial pressure of acetylene or ethylene in the inlet stream causes a variation of hydrogen partial pressure in the gradientless reactor. To diminish these variations, each change of acetylene or ethylene pressure was accompanied with an appropriate modification of the flow rate of the reacting mixture as it was proposed previously [38]. This procedure decreased the variations of hydrogen pressure to 0.56–0.78 kPa. The effect of this residual variation on the measured relation $r_i = f(p_{\mathrm{C_2H_2}})$ was minimised by expressing experimental results as the rates divided by hydrogen pressure, i.e., as $r_{\mathrm{C_2H_2}}/p_{\mathrm{H_2}}$, $r_{\mathrm{C_2H_6}}/p_{\mathrm{H_2}}$ and $r_{\mathrm{C_4}}/p_{\mathrm{H_2}}$. (The idea of dividing the rate by hydrogen pressure was described previously [38] and it is based on generally accepted assumptions that at low partial pressures of hydrogen the reactions of acetylene and ethylene hydrogenation are approximately first order with respect to hydrogen [1,10,40–45].)

3. Results and discussion

Figure 1 shows the hydrogenation of pure acetylene and acetylene in large excess of ethylene. The relations for acetylene–ethylene mixtures, presented in figure 1 (A), (B), (D), and (F), are compared with these for pure acetylene shown in figure 1 (C) and (F). It is seen in these figures that large excess of ethylene hardly affects hydrogenation of acetylene whereas small amounts of acetylene strongly affect hydrogenation of ethylene. The hydrogenation of pure acetylene (figure 1 (C) and (F)) leads mainly to ethylene while only small amounts of ethane and C_4 hydrocarbons are formed. During the hydrogenation of acetylene–ethylene mixtures (figure 1 (A), (B), (D), and (E)) at low partial pressure of acetylene a significant quantity of ethane is produced, mainly from ethylene. With increase of the pressure of acetylene the reaction slows down and at high pressure of acetylene the hydrogenation of acetylene appears to predominate over the hydrogenation of ethylene.

In figure 2, a summary of the kinetic studies is given. The rates of the reactions are expressed as turnover frequencies ($\mathrm{TOF_{C_2H_2}}$ – rate of acetylene consumption, $\mathrm{TOF_{C_2H_6}}$ – rate of ethane production, and $\mathrm{TOF_{C_4}}$ – rate of C_4 hydrocarbon production). Both the hydrogenation of acetylene and production of C_4 hydrocarbons vary similarly with acetylene pressure. Being independent of ethylene pressure in the range 0–40 kPa, both reaction rates increase with the pressure of acetylene up to about 0.02 kPa, and then slowly diminish. These results show that the sites involved in these reactions are not covered by ethylene for all ethylene pressures, and are insignificantly covered with acetylene at low pressures and almost fully covered at high pressure of acetylene. The fact that the coverage of sites by ethylene is negligible also at low pressures of acetylene leads to the assumption that the sites represent small spaces of the palladium surface between carbonaceous deposits (**A** sites) sterically inaccessible to ethylene [22,23]. Consequently it is assumed that hydrogenation of ethylene to ethane takes place on large palladium spaces between carbonaceous deposits (**E** sites), where ethylene is competitively adsorbed with acetylene. At low acetylene pressuret ($<$0.01 kPa) and at high ethylene pressure ($>$20 kPa), the effective reaction order ($\mathrm{TOF_{C_2H_6}}/p_{\mathrm{H_2}}$) with respect to ethylene is significantly lower than one. This result is in line with the assumption that two types of active sites are involved in the hydrogenation of acetylene–ethylene mixtures. It indicates that the coverage of **E** sites by ethylene is not negligible as it is in the case of **A** sites.

Figure 3 shows a simplified representation of the proposed model of the palladium surface covered by carbonaceous deposits in the course of hydrogenation of the acetylene–ethylene mixture. The model describes well the results of this work as well as results reported in the literature [7–9,11,18–23,45–53]. The carbonaceous deposits are composed of primary adsorbed acetylene species and surface polymeric species $\mathrm{C}_x\mathrm{H}_y$. Two types of catalytic sites, created on the palladium surface by carbonaceous deposits, are discriminated: **A** sites representing small palladium spaces and **E** sites representing large palladium spaces remained between carbonaceous deposits. It is postulated that **A** sites are accessible only to hydrogen and acetylene. It is also assumed that **A** sites are active only in hydrogenation and hydrooligomerisation of acetylene. Finally, the sites are supposed to be so small that they are inaccessible to adsorption and, by that, unable to hydrogenate ethylene.

The role of carbonaceous species in the formation of the palladium catalyst appears similar to so-called “modifiers” of the catalyst, such as Pb [54,55], B [54,56], Cu [11], and Au [11]. The role of the “modifiers” consists in creation of suitable palladium ensembles of unique adsorption and catalytic properties. The examination performed for the Pd(111) plane of a single crystal covered by the modifiers showed that: (i) a new weakly bound form of adsorption of acetylene appears, which is absent on the clean Pd(111) surface; (ii) modifiers cause decreasing of the surface coverage with ethylene; (iii) modifiers cause increasing of the selectivity of semihydrogenation of acetylene [11,54–56] or other alkynes [55,56]; (iv) modifiers cause increasing of selectivity of acetylene hydrogenation to ethylene in the

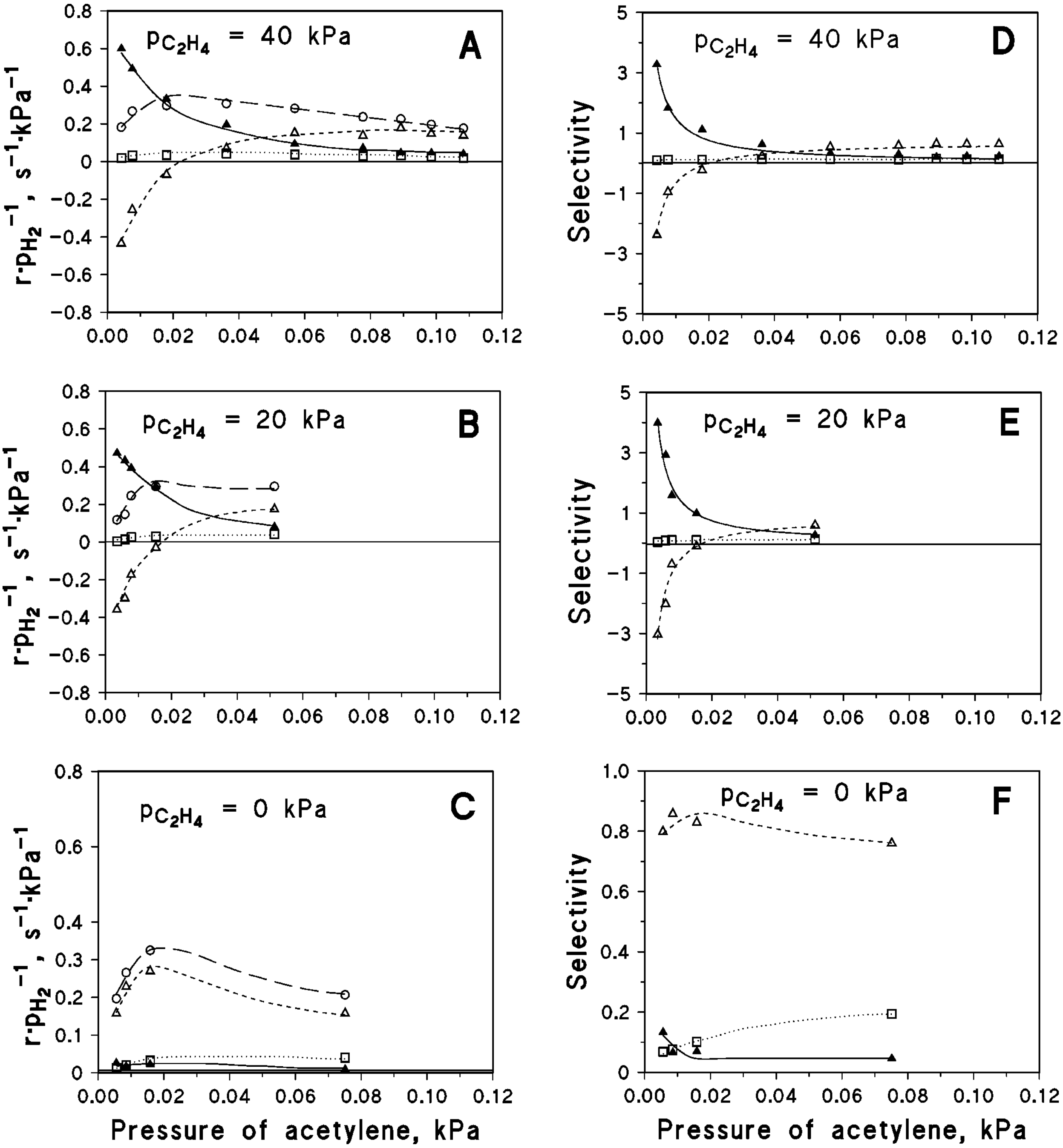

Figure 1. Kinetics of hydrogenation of acetylene and acetylene–ethylene mixtures. (○) Conversion of acetylene, (▲) production of ethane, (△) production of ethylene, and (☐) production of C_4 hydrocarbons multiplied by two. Figures (A)–(C) show the rate of the reactions, r_i ($\mathrm{mol}_i\,\mathrm{mol}^{-1}_{\mathrm{Pd}_{\mathrm{bulk}}}\,\mathrm{s}^{-1}$), where i correspond to acetylene, ethane, ethylene, and C_4 hydrocarbons, respectively. Figures (D)–(F) show the overall selectivities ($S_{C_2H_6}$, $S_{C_2H_4}$, and S_{C_4}) of hydrogenation of acetylene and acetylene–ethylene mixtures; $p_{H_2} = 0.64 \pm 0.08$ kPa; $T = 343$ K.

acetylene–ethylene mixture [54]. Based on the results of this work and the literature information [11,23,45–52], it may be assumed that vinylidene adspecies $(=C=CH_2)_{ad}$ is weakly adsorbed between the deposits and, in consequence, the reactive form of the acetylene.

In the proposed mechanism (see figure 3), it has been assumed that vinylidene molecule adsorbed on **A** sites is a key intermediate in acetylene hydrogenation, while π-bonded ethylene adsorbed on **E** sites is a key intermediate in ethylene hydrogenation. The second assumption is consistent with recently published results of Cremer et al. [53]. The authors used infrared–visible sum frequency generation to monitor the surface vibrational spectrum *in situ* during ethylene hydrogenation on Pt(111) at high total pressure (near 1 atm) and at temperature 295 K. Under the reaction conditions an ethylidyne overlayer adsorbed on three-fold sites covered the metal surface. The saturation coverage of ethylidyne was 0.25 monolayer. The authors discovered, that

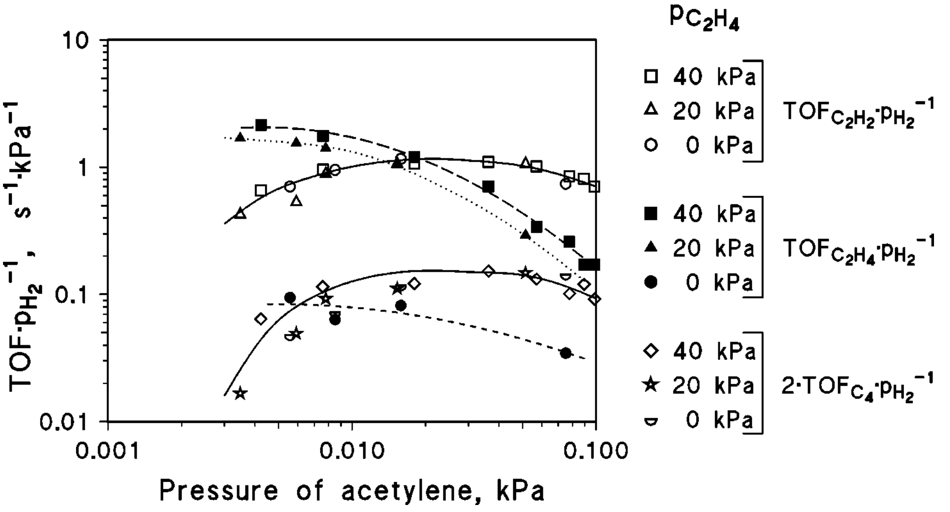

Figure 2. The summary of the effect of acetylene and ethylene partial pressures on hydrogenation of acetylene and acetylene–ethylene mixtures. The experimental conditions are as those in figure 1.

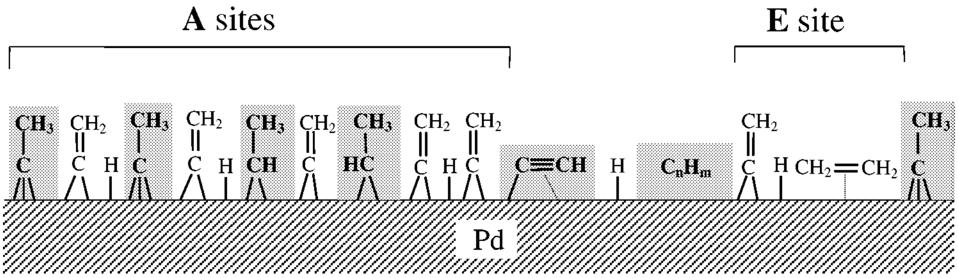

Figure 3. The simplified representation of the palladium catalyst surface during hydrogenation of the acetylene–ethylene mixture. The carbonaceous deposits creating sites **A** and **E** are represented by shaded rectangles. The reacting forms of acetylene, ethylene, and hydrogen are between the deposits.

in spite of expected large steric hindrance, a small amount of π-bonded ethylene (4% of monolayer) might adsorb on Pd surface atoms between the ethylidyne overlayer. The π-bonded ethylene is found to be a key intermediate in ethylene hydrogenation, whereas ethylidyne is only a spectator species not involved in ethylene hydrogenation.

A larger steric hindrance of the adsorbed ethylene molecule than of the adsorbed acetylene molecule is caused by the difference in the position of the C=C axis of the adsorbed molecule in respect to the Pd surface and by the larger number of hydrogen atoms in the ethylene molecule. In the π-bonded ethylene molecule, the C=C axis is parallel to the palladium surface (flatly lying) [52], whereas in adsorbed acetylene, as vinylidene molecule, it is perpendicular [48] or tilted [49] with respect to the surface.

Calculation of the relative sizes of adsorbed molecules of π-bonded ethylene and vinylidene supports the above conclusion as to a larger steric hindrance in adsorption of ethylene than acetylene. The bonds lengths and angles in ethylene gaseous molecule were used to calculate the size of adsorbed molecules of π-bonded ethylene and vinylidene (the carbon–carbon double bond length is equal to 1.334 Å, the carbon–hydrogen length is 1.08 Å, van der Waals radius of hydrogen atom is 1.2 Å, van der Waals radius of carbon atom is about 3.1 Å and the angle H–C–H is 116° [57]). For π-bonded ethylene, the length and width of the molecules in cross section parallel to the metal surface, are equal to 3.82 and 3.76 Å, respectively. For vinylidene, the length and width of the molecule in cross section perpendicular to the C=C axis are: 3.82 and about 3.1 Å, respectively. It means that acetylene may adsorb between the carbonaceous deposits, on narrow surface domains of about 3.1 Å in size (the size of van der Waals radius of carbon atom), whereas ethylene needs wider sizes, at least 3.76 Å.

The assumption of larger steric hindrance of the adsorbed ethylene molecule than of the adsorbed acetylene molecule, is also in agreement with the fact that fractional maximum surface coverage of vinylidene on Pd(111) is larger than for flatly lying ethylene at low temperature (they are equal to 1 [48] and 0.3 [52], respectively).

The accessibility of **E** sites to all molecules might suggest that the sites are active not only in ethylene hydrogenation but also in the conversion of acetylene to ethylene, ethane, and C_4 hydrocarbon. However, the suggestion seems improbable as the experimental results of this work show that ethylene, in spite of its competitive adsorption on **E** sites, does not influence $TOF_{C_2H_2}/p_{H_2}$ and TOF_{C_4}/p_{H_2} (see figure 2). These results indicate that the population of **E** sites in fully stabilised catalyst is low [12,13,22,23] and that specific activity of **E** sites in hydrogenation of acetylene is similar as that on **A** sites. Consequently conversion of acetylene and the limiting step of formation of C_4 hydrocarbons proceed mainly on inaccessible to ethylene **A** sites. On the other hand, hydrogenation of ethylene proceeds on rather scarce **E** sites and competitive adsorption of acetylene with ethylene on the sites explains the observed decrease of $\mathrm{TOF}_{C_2H_6}/p_{H_2}$ with the pressure of acetylene. The selectivity of the hydrogenation of acetylene–ethylene mixtures to ethane, $S_{C_2H_6}$, decreases with $p_{C_2H_2}$ (figure 1 (D) and (E)), as the result of competitive adsorption of acetylene with ethylene on **E** sites and rapid decrease of the rate of hydrogenation of ethylene to ethane. Simultaneously, the rate of acetylene conversion increases or slowly decreases. At higher $p_{C_2H_2}$ (>0.03 kPa) the catalyst is very selective ($S_{C_2H_4}$ is high).

The model of the catalyst surface that is proposed in this work is similar to that reported before for other Pd/α-Al_2O_3 catalyst [23]. However, previously we discriminated two kinds of **A** sites: $\mathbf{A}_1$ sites representing small palladium ensembles that are free of carbonaceous deposits and $\mathbf{A}_2$ sites representing palladium ensembles that are fully covered by the deposits. Such discrimination reflected two mechanisms of hydrogenation of acetylene. In the first case, the reaction concerns acetylene and hydrogen coadsorbed on palladium, while in the second case the reaction occurs between acetylene that is adsorbed reversibly in the "second layer" with hydrogen transferred from carbonaceous deposits. The second mechanism has been introduced after Webb et al. [7–9], who assumed that adsorption in the "second layer" occurs on the top of the first one. However, the exact mechanism of this reaction is still open to discussion [1,11–13,20,24,25,45]. An insight into this problem has been obtained from the studies of the temperature effect on the acetylene hydrogenation [23,58]. These examinations show that apparent activation energy of the reaction on $\mathbf{A}_2$ sites is close to that related on $\mathbf{A}_1$ sites, which suggests that $\mathbf{A}_1$ sites and $\mathbf{A}_2$ sites are identical in their kinetic nature. This suggestion is also consistent with large differences in selectivities of acetylene hydrogenation in presence of ethylene observed on various transition metals although carbonaceous deposits cover all of them [8,9]. Recent results [20,22] showed that the type of coke formed on the palladium catalyst during catalyst stabilisation in the reaction conditions of hydrogenation of acetylene–ethylene mixture, depends on reaction condition and has a large influence on the selectivity of unwanted formation of ethane. However, the coke composition was not directly related to the selectivity of the catalyst at a standard gas-phase composition [20]. So, these facts suggest that the most important parameter is the geometrical structure of the deposits on the metal surface, which has influence on the relative population of small and large palladium ensembles between the deposits. The effect depends on both the type of metal and the conditions of the reaction during the catalyst stabilisation. It is also suggested that the previously distinguished $\mathbf{A}_2$ sites concern in reality hydrogenation of acetylene adsorbed on palladium with the use of hydrogen transfer from nearby carbonaceous deposits adsorbed on the metal. In the present model, it is postulated that acetylene is adsorbed as vinylidene on **A** sites between strongly adsorbed carbonaceous deposits [11,45,48,49]. The hydrogenation of the vinylidene occurs with use of coadsorbed hydrogen (competitive path of the reaction responsible for observed maximum on relation $r_{C_2H_2}/p_{H_2} = f(p_{C_2H_2})$) and hydrogen transferred from nearby carbonaceous deposits (non-competitive path of the reaction). The proposed model of the catalyst surface suggests that the selectivity of hydrogenation of acetylene to ethylene in ethylene-rich feedstock may be improved by a selective poisoning of **E** sites. The poison should be too bulky for adsorption on **A** sites, but ought to be irreversibly adsorbed on **E** sites.

Figure 4 (A)–(C) shows selectivity of hydrogenation of acetylene–ethylene mixture and acetylene alone to various

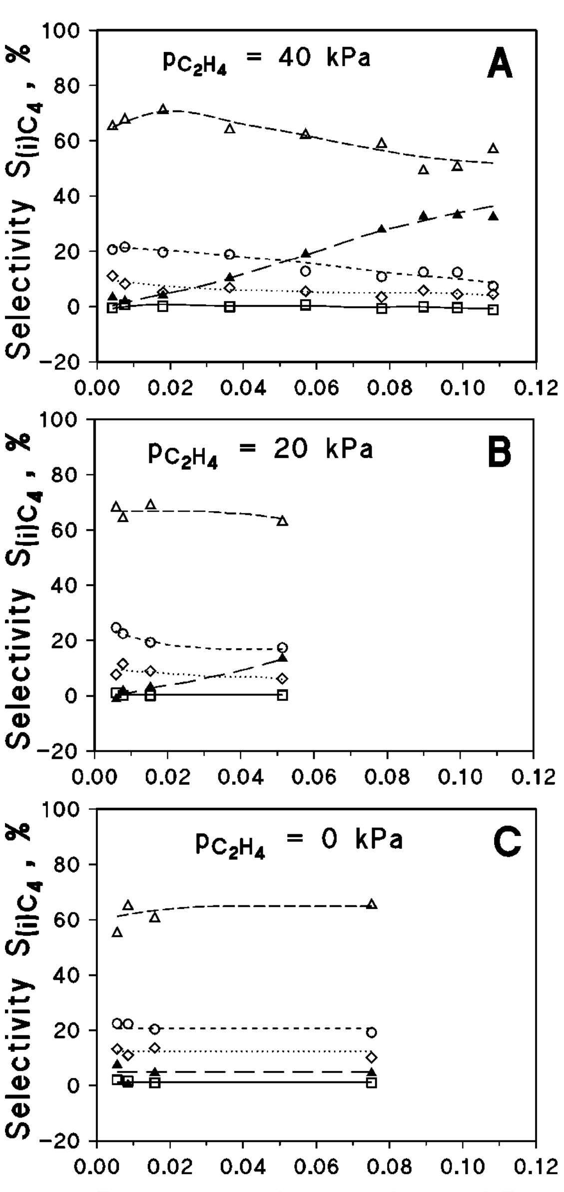

Figure 4. Selectivity of various C_4 hydrocarbons ($S_{(i)C_4}$) for hydrogenation of acetylene and acetylene–ethylene mixtures. The experimental conditions are as those in figure 1. (□) *n*-butane, (△) 1-butene, (▲) 1,3-butadiene, (○) *trans*-2-butene, and (◇) *cis*-2-butene.

C_4 hydrocarbons, defined as

$$S_{(i)\mathrm{C}_4} = \frac{r_{(i)\mathrm{C}_4}}{r_{\mathrm{C}_4}} \times 100, \qquad (7)$$

where $i = 1$–5 correspond to formation of n-butane, 1-butene, *trans*-2-butene, *cis*-2-butene, and 1,3-butadiene, respectively. The presented relations appear to contain valuable information on the mechanism of the formation of C_4 hydrocarbons. It is supposed that 1,3-butadiene is a primary C_4 hydrocarbon product formed by hydrooligomerisation of two vinylidene species adsorbed on **A** site [11,45] and that this is the limiting step of the rate of hydrocarbon formation. The rate of this reaction is not influenced by ethylene pressure; it agrees with the fact that ethylene is not adsorbed on **A** sites. Further, it is supposed that n-butenes and n-butanes are formed by hydrogenation of 1,3-butadiene. The reaction very likely occurs on **E** sites and the transport of 1,3-butadiene may proceed by gas phase or by diffusion over the catalyst surface. With increase of pressure of acetylene and/or ethylene the **E** sites active in this reaction are blocked. This leads to an increase of selectivity to butadiene and decrease of selectivity to butenes.

It has been shown [59], that the derived rate equations, consistent with the proposed mechanism of hydrogenation of acetylene–ethylene mixtures on **A** and **E** sites, fit the experimental data very well. A statistical analysis of regression using the experimental data for the derived kinetic model and models presented in the literature shows that our model fits experimental data best.

4. Conclusions

Two types of sites (**A** and **E**) were identified for the commercial C-31-1A catalyst from CCI (0.038% Pd/α-Al_2O_3) for hydrogenation of traces of acetylene in ethylene-rich feedstock. It was proposed that two types of catalytic sites are created on the palladium surface by carbonaceous species deposited during the reaction: **A** sites representing small palladium spaces and **E** sites representing large palladium spaces between the carbonaceous species. The **A** sites adsorb acetylene and hydrogen but, due to steric hindrance, do not adsorb ethylene. The **A** sites are involved in conversion of acetylene, producing mainly ethylene and small amounts of ethane, and butadiene. The **E** sites adsorb all reagents; they are responsible for hydrogenation of ethylene to ethane and of butadiene to n-butenes and n-butane. Selectivity of the catalyst depends on the proportions and specific activities of **A** and **E** sites.

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