The effect of palladium particle size on the kinetics of hydrogenation of acetylene–ethylene mixtures over Pd/SiO$_2$ catalysts

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Received 25 April 2000; accepted 17 October 2000

The kinetics of hydrogenation of acetylene–ethylene mixtures over the Pd/SiO$_2$ catalysts has been studied over a wide range of Pd particle sizes ($d = 42$–262 Å). The size d was found to have no influence on the mechanism of the reaction and on the adsorption strengths of acetylene and ethylene molecules (the electronic effect was not observed to occur). The observed antipathetic structure sensitivity originates from two geometric effects: (i) statistics of faces in Pd crystallites, (ii) surface-site statistics in the crystallite faces carrying carbonaceous deposits. A general kinetic model of hydrogenation of acetylene–ethylene mixtures on Pd/SiO$_2$ catalysts has been developed. The model describes the relation of turnover frequency to size d at various partial pressures of the reactants.

KEY WORDS: hydrogenation of acetylene–ethylene mixtures; palladium catalysts; carbonaceous deposits; effect of metal particles size; kinetic model

1. Introduction

The effect of metal particle size d in supported metal catalysts on the rate of the reaction has been extensively investigated and reviewed [1,2]. Most investigations have been confined to the relation between turnover frequency (TOF) and size d at fixed partial pressures of the reactants and temperature. So far this relation has been very little looked into, especially as regards the effect of d on a complete kinetic equation. This paper is focused on catalytic hydrogenation of acetylene in excess of ethylene, an important industrial process [3–7]. TOF in the hydrogenation of alkynes over supported palladium catalysts increases as d is increased up to 40 Å [6–18]. This antipathetic structure sensitivity [1] has been ascribed to electron deficiency in small Pd particles (the electronic effect). This paper sets out to describe how d affects the mechanism and kinetics of hydrogenation of acetylene–ethylene mixtures over Pd/SiO$_2$ catalysts over a wide range of d. The effect of d on the parameters of the kinetic model recently proposed for Pd/α-Al$_2$O$_3$ ($d = 43.6$ Å) [19,20] has been determined.

2. Experimental

2.1. Materials

Table 1 summarises the silica-supported catalysts examined. The 2.6% Pd/SiO$_2$ catalyst (SE$_{2.6}$) was prepared at the Laboratoire de Réactivité de Surface et Structure at Université P. et M. Curie, Paris, by following the procedure described in detail by Bouchemova [15]. The catalyst was obtained by the exchange between the $[Pd(NH_3)_4]_2^+$ and the NH_4^+ cations attached to the SiO group in the support. To obtain a series of catalysts endowed with large palladium particles, the SE$_{2.6}$ catalyst was calcined in oxygen at various temperatures (673–1173 K). In this way, four modified catalysts (1SE$_{2.6}$, 2SE$_{2.6}$, 3SE$_{2.6}$ and 4SE$_{2.6}$) were prepared.

Prior to palladium dispersion measurements and kinetic studies, the catalysts were subjected to the standard *in situ* pretreatment involving: (i) calcination in an oxygen stream (20 ml min^{-1}) at 573 K for 0.5 h, (ii) reduction in hydrogen stream (20 ml min^{-1}) at 573 K for 1 h, and (iii) desorption of hydrogen in helium stream (20 ml min^{-1}) at 723 K for 1 h. Then, the samples were cooled to 353 K in flowing He.

Cylinder gases: ethylene (MZPiR, Poland, 99.96%), helium (Plasco, 99.99%), hydrogen (AgaGas, 99.999%) and acetylene (Matheson, 99.6%) were used. Each gas was purified in a series of columns packed subsequently with Cu/SiO$_2$, silica gel and a 5A molecular sieve.

2.2. Catalyst characterisation

The metal fraction exposed (FE) was measured by the oxygen chemisorption method, similarly as before [19]. The

Table 1
Characteristics of Pd/SiO$_2$ catalysts.

Catalyst	Pd loading (wt%)	Precalcination		FE[a]	d[b] (Å)
		Temperature (K)	Time (h)		
SE$_{2.6}$	2.6	–	–	0.288	42
1SE$_{2.6}$	2.64	673	1	0.247	51
2SE$_{2.6}$	2.72	773	1	0.186	74
3SE$_{2.6}$	2.88	873	1	0.0848	162
4SE$_{2.6}$	3.13	973	1	0.0525	262

[a] Fraction exposed, determined by oxygen chemisorption at 273 K.
[b] Calculated from FE and relations (1) and (2).

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average metal particle size (d) was calculated by using the following general relations valid for common metal catalysts [21]:

$$d = \frac{5.01 d_{\mathrm{at}}}{\mathrm{FE}} \quad \text{at FE} < 0.2, \tag{1}$$

$$d = \frac{3.32 d_{\mathrm{at}}}{\mathrm{FE}^{1.23}} \quad \text{at } 0.2 \leqslant \mathrm{FE} \leqslant 0.92, \tag{2}$$

where d_{at} is the diameter of the metal atom (2.74 Å for Pd atom).

Table 1 lists FE and d for the pretreated Pd/SiO_2 catalysts, prior to catalytic screening.

2.3. Apparatus for hydrogenation of acetylene–ethylene mixtures

The reaction was carried out in an all-glass no-grease flow system equipped with a gradientless microreactor [22]. The inlet mixtures of 39.5% C_2H_4, 0.76% H_2, 0.01–0.294% C_2H_2 and He in balance were prepared continuously by using flow control valves and microdispensers of hydrogen and acetylene [23]. This method allows low concentrations of C_2H_2 and H_2 to be obtained in the stream of the reaction mixture at a flow rate of 34 ml min^{-1}. The compositions of both the inlet and outlet streams were measured by a Giede GCHF 18.3 gas chromatograph provided with a flame ionisation detector, equipped with a 1 m long column packed with silica gel. The column was operated at 353 K with argon as a carrier gas.

2.4. Kinetic studies

The kinetic studies on hydrogenation of acetylene–ethylene mixtures were carried out by using finely powdered catalyst samples (0.004–0.015 g) to avoid any influence of internal diffusion. After having been given the standard *in situ* pretreatments (see section 2.1.), the catalyst was stabilised under the reaction conditions by passing the reaction mixture of 0.294% C_2H_2, 39.5% C_2H_4 and 0.76% H_2 in He through the catalyst bed at a temperature of 353 ± 0.2 K for about 19 h. After the stabilisation had been performed, the kinetic studies were started on hydrogenation of acetylene–ethylene mixtures. The kinetic measurements consisted of measuring the rate of acetylene consumption and the rate of ethane production over a wide range of partial pressures of acetylene, $p_{C_2H_2}$, over the catalyst, at a chosen temperature. This was attained by varying from run to run the partial pressure of acetylene in the inlet stream [24]. The total flow rate of, and the content of ethylene and hydrogen in, the inlet stream were kept unchanged during the kinetic measurements (34 ml min^{-1}, 39.5% C_2H_4 and 0.76% H_2, respectively). Varying the percentage of acetylene in the inlet stream resulted in a modified hydrogen partial pressure in the reactor, p_{H_2}; this was evaluated from the acetylene consumption and the ethane formation rates. The partial pressures of acetylene, hydrogen and ethylene in the reactor were varied within the ranges 0.0059–0.285 kPa, 0.27–0.77 kPa and 39.1–40.3 kPa, respectively. Chromatographic analyses of the inlet and outlet streams were used to establish the data for the determination of the reaction rates, which were expressed as the turnover frequencies: $\mathrm{TOF}_{C_2H_2}$ – the rate of acetylene disappearance expressed as mol C_2H_2 per mol of surface Pd atoms per s; $\mathrm{TOF}_{C_2H_6}$ – the rate of ethane production expressed as mol C_2H_6 per mol of surface Pd atoms per s. The effect of variation of p_{H_2} on the observed relations $\mathrm{TOF}_{C_2H_2} = f(p_{C_2H_2})$ and $\mathrm{TOF}_{C_2H_6} = f(p_{C_2H_2})$ was minimised by normalising the experimental results vis., by dividing the rates by the hydrogen pressure, i.e.: $\mathrm{TOF}_{C_2H_2}/p_{H_2}$ and $\mathrm{TOF}_{C_2H_6}/p_{H_2}$. This procedure was explained in detail elsewhere [24] (the reactions are approximately first order with respect to hydrogen).

The overall selectivities of the hydrogenation of acetylene in acetylene–ethylene mixtures were defined as [25]

$$S = \frac{\mathrm{TOF}_{C_2H_2}}{\mathrm{TOF}_{C_2H_2} + \mathrm{TOF}_{C_2H_6}}. \tag{3}$$

3. Results and discussion

The results of the stabilisation of the catalysts in the reaction conditions are presented in figure 1. The activities of the catalysts increased by about 30% as the time on stream (TOS) was protracted, and attained a steady state in 6 h (stabilisation of the catalysts was continued up to 19 h to ensure they are stable under the reaction conditions).

The results of the kinetic measurements of the steady state process (figure 2) demonstrate that the effects of $p_{C_2H_2}$ on $\mathrm{TOF}_{C_2H_2}/p_{H_2}$ and on the overall selectivity observed on Pd/SiO_2 catalysts are similar to those observed previously for the Pd/α-Al_2O_3 catalysts [19,25] although the former differed from the latter in type of the support and in d. These results suggest that also the reaction mechanisms are identi-

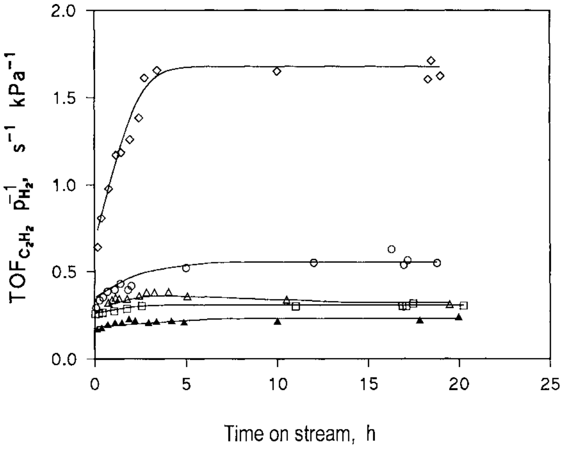


Figure 1. $\mathrm{TOF}_{C_2H_2}/p_{H_2}$ versus time on stream for the Pd/SiO_2 catalysts. $p_{C_2H_2} = 0.14$–0.32 kPa, $p_{C_2H_4} = 39.6 \pm 0.3$ kPa and $p_{H_2} = 0.3$–0.6 kPa; temperature of reaction (T) 353 ± 0.2 K. Catalysts: (▲) $SE_{2.6}$ $d = 42$ Å, (△) $1SE_{2.6}$ $d = 51$ Å, (□) $2SE_{2.6}$ $d = 74$ Å, (○) $3SE_{2.6}$ $d = 162$ Å and (◇) $4SE_{2.6}$ $d = 262$ Å.

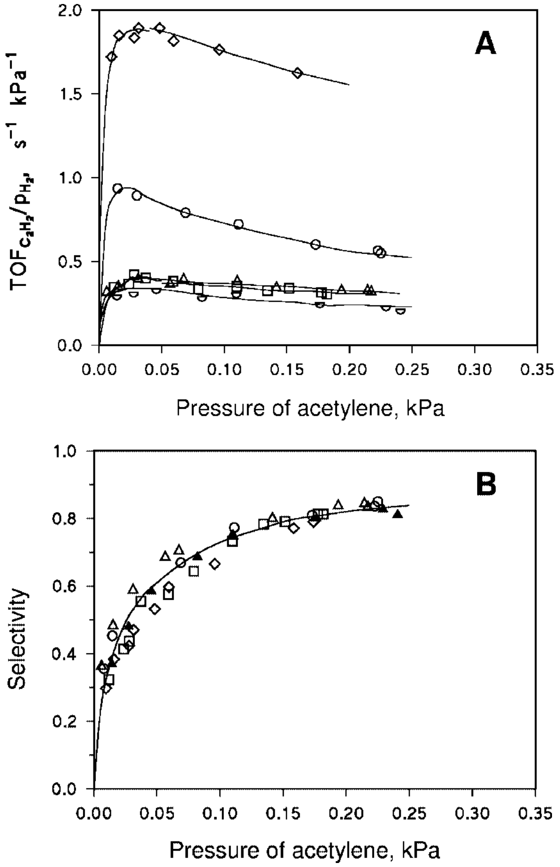


Figure 2. The kinetics of hydrogenation of acetylene–ethylene mixtures over the Pd/SiO$_2$ catalysts: (A) $\mathrm{TOF}_{C_2H_2}/p_{H_2}$ versus $p_{C_2H_2}$; catalysts: (◒) SE$_{2.6}$ $d = 42$ Å, (△) 1SE$_{2.6}$ $d = 51$ Å, (□) 2SE$_{2.6}$ $d = 74$ Å, (○) 3SE$_{2.6}$ $d = 162$ Å and (◇) 4SE$_{2.6}$ $d = 262$ Å. (B) S versus $p_{C_2H_2}$; catalysts: (▲) SE$_{2.6}$ $d = 42$ Å, (△) 1SE$_{2.6}$ $d = 51$ Å, (□) 2SE$_{2.6}$ $d = 74$ Å, (○) 3SE$_{2.6}$ $d = 162$ Å and (◇) 4SE$_{2.6}$ $d = 262$ Å. $p_{C_2H_4} = 39.8 \pm 0.6$ kPa, $p_{H_2} = 0.3$–0.6 kPa, $T = 353 \pm 0.2$ K.

Table 2

Apparent activation energies ($E_{a(C_2H_2)}$) for hydrogenation of acetylene over SE$_{2.6}$ catalyst.[a]

$p_{C_2H_2}$ (kPa)	T (K)	$\mathrm{TOF}_{C_2H_2}/p_{H_2}$ (kPa^{-1} s^{-1})	$E_{a(C_2H_2)}$ (kJ mol^{-1})
0.15	353	0.2830	63.2 ± 4.6
	333	0.0896	
	318	0.0264	
0.10	353	0.309	61.6 ± 0.02
	333	0.0864	
	318	0.304	
0.05	353	0.300	62.6 ± 6.7
	333	0.0672	
	318	0.0278	

[a] Reaction conditions: $p_{C_2H_2} = 40.5 \pm 0.2$ kPa, $p_{H_2} = 0.58 \pm 0.2$ kPa, $d = 42$ Å.

cal and that the kinetic model proposed for the Pd/α-Al$_2$O$_3$ catalyst [19,20] is applicable to the Pd/SiO$_2$ catalysts.

Detailed studies on the effect of temperature on $\mathrm{TOF}_{C_2H_2}/p_{H_2}$ for catalysts SE$_{2.6}$ showed the apparent activation energy of acetylene hydrogenation ($E_{a(C_2H_2)}$) to be about 62 kJ mol^{-1} (table 2). The values of $E_{a(C_2H_2)}$ are in reasonable agreement with those reported [6,7] (58.6–71.1 kJ mol^{-1}) for acetylene hydrogenation over various Pd/Al$_2$O$_3$ catalysts carried out at a high total pressure. It is interesting that $E_{a(C_2H_2)}$ is almost independent of d and $p_{C_2H_2}$.

The rate of acetylene hydrogenation ($\mathrm{TOF}_{C_2H_2}/p_{H_2}$) on Pd/SiO$_2$ catalysts strongly increases with d (figure 2(A)). The results (figure 2 and table 2) cannot be explained by the electronic effect [6–21,26] because: (i) the measured $\mathrm{TOF}_{C_2H_2}/p_{H_2}$ is approximately proportional to d up to at least 262 Å, whereas Pd crystallites reportedly acquire electronic properties of the bulk metal at d greater than about 50 Å [1,8–10], (ii) changes in electron deficiency of metal particles with d should influence the competitive adsorption of acetylene and ethylene and thus should strongly affect S, whereas the measured S is seen to be almost independent of d (figure 2(B)); (iii) the decrease of adsorption equilibrium constant of acetylene with d should shift the maximum in the relation $\mathrm{TOF}_{C_2H_2}/p_{H_2} = f(p_{C_2H_2})$ towards higher $p_{C_2H_2}$, whereas experimentally the position of the maximum is seen to remain unaffected (figure 2(A)); (iv) changes in electron deficiency of metal particles with d should also influence $E_{a(C_2H_2)}$, whereas the results shown in table 2 and the results of industrial-like hydrogenation of acetylene [6,7] have shown $E_{a(C_2H_2)}$ to be practically independent of d. Consequently, the present kinetic results indicate that the geometric effect plays an important role in the hydrogenation of acetylene–ethylene mixtures over Pd/SiO$_2$ catalysts. Therefore, the general kinetic model proposed assumes the observed structure sensitivity to be due to the average surface concentration of active sites increasing as the particle size is increased, which affects the frequency factors of the rate constants but neither influence the mechanism of the reaction nor the adsorption strengths of acetylene and ethylene molecules. These assumptions are consistent with the activity "scaling law" proposed [27,28] for various catalytic systems, but so far this law has not been considered for the hydrogenation of highly unsaturated hydrocarbons. For many reactions occurring on the supported metal catalysts at a given temperature and partial pressures of reactants, the relation between TOF and d has been found describable by the following equation:

$$\mathrm{TOF} \propto d^{(D_R-2)}, \tag{4}$$

in which D_R, "the reaction dimension", is the characteristic parameter of the catalytic system, quantifying the structure sensitivity in dispersed catalysts.

Accordingly, relation (4) is applied to the kinetic model proposed recently for the Pd/α-Al$_2$O$_3$ catalyst [20]. Two types of active sites have been suggested to be formed on the palladium surface by the carbonaceous deposits: the A sites, where only acetylene is converted, and the E sites where ethylene is hydrogenated. The A sites adsorb acetylene and hydrogen but, owing to steric hindrance, do not adsorb ethylene. The deposits also act as a transmitter of hydrogen atoms towards the reacting molecules of acetylene adsorbed on sites A.

In the present model, three main reactions were considered:

$$C_2H_4 + H_2 \rightarrow C_2H_6$$
$$\text{Langmuir–Hinshelwood mechanism (on sites E)}, \tag{5}$$
$$C_2H_2 + H_2 \rightarrow C_2H_4$$
$$\text{hydrogen transfer mechanism (on sites A)}, \tag{6}$$
$$C_2H_2 + H_2 \rightarrow C_2H_4$$
$$\text{Langmuir–Hinshelwood mechanism (on sites A)}. \tag{7}$$

In addition to reactions (5)–(7), in the kinetic model for the Pd/α-Al_2O_3 catalysts two minor, viz., conversions of acetylene to ethane and to C_4-hydrocarbons, were taken into account. In this work these minor reactions were neglected to minimise the number of parameters in the general model proposed, which takes into account not only the effect of partial pressures of the reactants but also the effect of d.

It is assumed that: (i) changes in the reaction rates with d are caused by changes in the respective rate constants in the applied kinetic model [20] according to equation (4), (ii) the reaction dimensions for reactions (6) and (7), proceeding on the same type of active sites (on sites A), are the same:

$$D^A_{R(d)} = D^A_{R(L-H)} = D^A_R, \tag{8}$$

in which $D^A_{R(d)}$, $D^A_{R(L-H)}$ are the reaction dimensions for reactions (6) and (7), respectively; D^A_R is the reaction dimension for hydrogenation of acetylene.

Taking into account equations (4) and (8) and the kinetic model proposed for the Pd/α-Al_2O_3 catalyst [20], the general kinetic model for the various Pd/SiO_2 catalysts may be expressed by the following equations at the fixed ethylene partial pressure ($p_{C_2H_4}$):

$$\frac{\mathrm{TOF}_{C_2H_2}}{p_{H_2}} = (d_{\mathrm{rel}})^{(D^A_R-2)} \times \left(\frac{k^0_d p_{C_2H_2}}{1+K^A_{C_2H_2}p_{C_2H_2}} + \frac{k^0_{L-H}p_{C_2H_2}}{(1+K^A_{C_2H_2}p_{C_2H_2})^2}\right), \tag{9}$$

$$\frac{\mathrm{TOF}_{C_2H_6}}{p_{H_2}} = (d_{\mathrm{rel}})^{(D^E_R-2)} \frac{k^0_E}{(1+K^E p_{C_2H_2})^3}, \tag{10}$$

$$S = \left(\frac{k^0_d p_{C_2H_2}}{1+K^A_{C_2H_2}p_{C_2H_2}} + \frac{k^0_{L-H}p_{C_2H_2}}{(1+K^A_{C_2H_2}p_{C_2H_2})^2}\right) \Big/ \left[\left(\frac{k^0_d p_{C_2H_2}}{1+K^A_{C_2H_2}p_{C_2H_2}} + \frac{k^0_{L-H}p_{C_2H_2}}{(1+K^A_{C_2H_2}p_{C_2H_2})^2}\right) + \frac{k^0_E}{(1+K^E p_{C_2H_2})^3}(d_{\mathrm{rel}})^{(D^E_R-D^A_R)}\right], \tag{11}$$

where

$$K^E = \frac{K^E_{C_2H_2}}{1+K^E_{C_2H_4}p_{C_2H_4}}, \tag{12}$$

$$k^0_E(d)^{(D^E_R-2)} = \frac{k_e p_{C_2H_4}}{(1+K^E_{C_2H_4}p_{C_2H_4})^3}, \tag{13}$$

in which d_{rel} is the relative metal particle size ($d_{\mathrm{rel}} = d/d_{\mathrm{at}}$); D^E_R is the reaction dimension for reaction (5) (proceeding on sites E); k^0_E is the apparent constant specific for reaction (5) (at fixed $p_{C_2H_4}$); k^0_d and k^0_{L-H} are the specific constants for the reactions (6) and (7), respectively; $K^E_{C_2H_2}$ and $K^E_{C_2H_4}$ are the adsorption constants of acetylene and ethylene on sites E, respectively; $K^A_{C_2H_2}$ is the adsorption constant of acetylene on sites A.

Table 3
Parameters adjusted to the kinetic model of acetylene conversion on Pd/SiO_2 catalysts.[a]

Model parameter	Value	Standard deviation
D^A_R	2.899	0.046
$K^A_{C_2H_2}$ (kPa^{-1})	67.1	19.4
k^0_d ($s^{-1}\,kPa^{-2}$)	1.03	0.44
k^0_{L-H} ($s^{-1}\,kPa^{-2}$)	4.91	1.36

[a] Reaction conditions: $p_{C_2H_2} = 0.0059$–0.28 kPa, $p_{C_2H_4} = 39.6 \pm 0.6$ kPa, $p_{H_2} = 0.27$–0.77 kPa, $T = 353$ K; $d = 42$–262 Å.

Table 4
Fitting parameters related to the kinetic model of ethane formation on Pd/SiO_2 catalysts.[a]

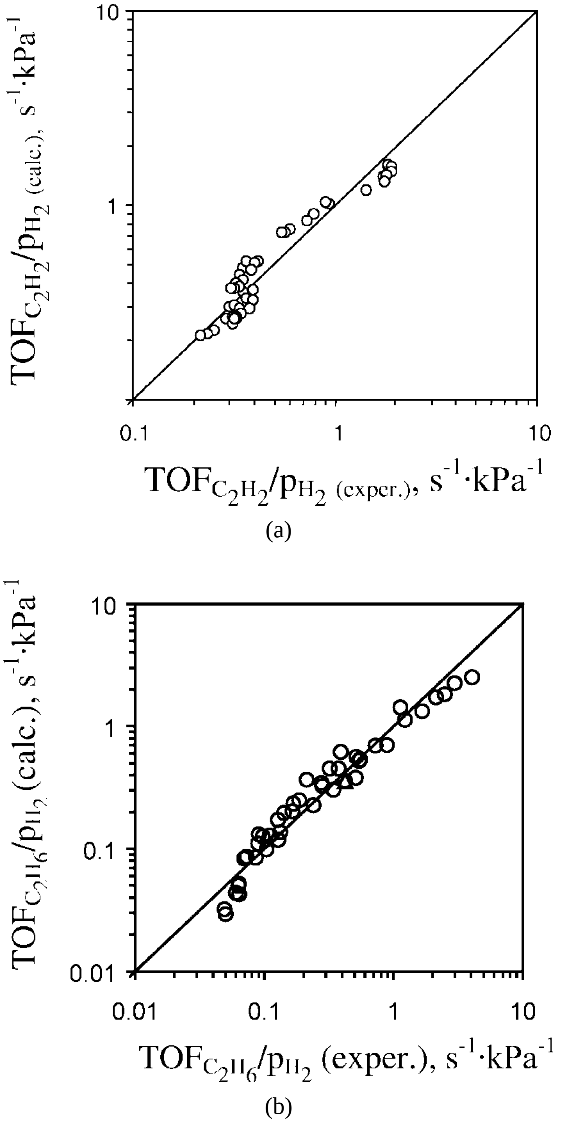
Model parameter	Value	Standard deviation
D^E_R	2.987	0.063
K^E (kPa^{-1})	6.51	0.50
k^0_E ($s^{-1}\,kPa^{-2}$)	0.0334	0.0082

[a] Reaction conditions: $p_{C_2H_2} = 0.0059$–0.285 kPa, $p_{C_2H_4} = 39.6 \pm 0.6$ kPa, $p_{H_2} = 0.27$–0.77 kPa, $T = 353$ K, $d = 42$–262 Å.

The parameters of the model estimated by the regression analysis based on the least squares method are shown in tables 3 and 4. The model proposed reproduces the experimental data very well (figure 3).

The calculation of the relations of the intrinsic reaction rates of acetylene hydrogenation versus $p_{C_2H_2}$ (for reactions (6) and (7)), by using equation (9), and the parameters estimated for the kinetic model, have shown that the contribution of the non-competitive path of acetylene hydrogenation (reaction (6)) increases as $p_{C_2H_2}$ is raised. At high $p_{C_2H_2}$, acetylene hydrogenation proceeds mainly via hydrogen transfer from deposits and this explains the zero order with respect to acetylene observed experimentally [3,28,32].

Figure 4 shows the relation $\mathrm{TOF}_{C_2H_2}/p_{H_2}$ versus d found for the Pd/SiO_2 catalysts under the same reaction conditions. A relation is seen to cover a wide range of d (in logarithmic scale) in agreement with the scaling law (equation (4)). Figure 4 shows also the recalculated results of Aduriz et al. [6,7] of acetylene–ethylene hydrogenation carried out on various Pd/Al_2O_3 catalysts under industrial conditions. The relations (1) and (2) were used to calculate d on the basis of the FE as determined by Aduriz et al. [6,7]. Actually, these results are also in agreement with the scaling law (the geometric effect), even if they have been in-



(a)

(b)

Figure 3. The parity plots: (a) calculated versus experimental $\mathrm{TOF}_{C_2H_2}/p_{H_2}$ for the Pd/SiO$_2$ catalysts; (b) calculated versus experimental $\mathrm{TOF}_{C_2H_6}/p_{H_2}$ for the Pd/SiO$_2$ catalysts; $p_{C_2H_2} = 0.0059$–0.285 kPa, $p_{C_2H_4} = 39.6 \pm 0.6$ kPa, $p_{H_2} = 0.27$–0.77 kPa, $T = 353 \pm 0.2$ K, $d = 42$–262 Å.

terpreted in terms of the electronic effect. The values of D_R estimated for hydrogenation of acetylene–ethylene mixtures are equal to about 3. The fact that values of D_R are higher than 2 may indicate that it is only the faces of palladium crystallites that are active [2,27,28]. For example, $D_R = 2.90 \pm 0.15$ has been determined [27] for methanation of CO over Pd/SiO$_2$ catalysts with d within the range 12–63 Å and interpreted by assuming that only the atoms in Pd (111) and (100) faces of a cubo-octahedron are active. Therefore, TOF can be assumed to be proportional to n_{pl}/n_s (where n_{pl} denotes the number of surface atoms in the faces, and n_s is the total number of surface atoms), and the theoretical D_R value could be calculated from the slope of the relation of $\log(n_{pl}/n_s) = f(\log(d))$ according to equation (4). The $D_R = 2.77 \pm 0.09$ calculated by using van Hardeveld and Hartog's surface atoms statistics [30] (denoted further as VH surface atoms statistics), was in good agreement with the experimental D_R. However, taking into account the experimental range of Pd crystallites for Pd/SiO$_2$ catalysts used in this work ($d = 42$–262 Å), this interpretation of high experimental D_R value cannot be directly applied. By applying the VH surface atoms statistics, Bennett and Che [2] have calculated the relation of $\log(n_{pl}/n_s) = f(\log(d))$ for a larger range of d (10–500 Å). They showed this relation not to be a straight line and that the D_R calculated (as the slope of this relation) decreases with d. Figure 4 shows the results of analogous calculations performed for the present experimental range of d. The calculated D_R (five filled black squares in figure 4) is equal to 2.114 ± 0.016. Therefore, it is significantly lower than the experimental D_R values estimated for acetylene and ethylene hydrogenation on the Pd/SiO$_2$ catalysts. Accordingly, the VH surface atoms statistics alone cannot quantitatively explain the observed antipathetic structure sensitivity of acetylene and ethylene hydrogenation, and consequently other geometric effects should be considered.

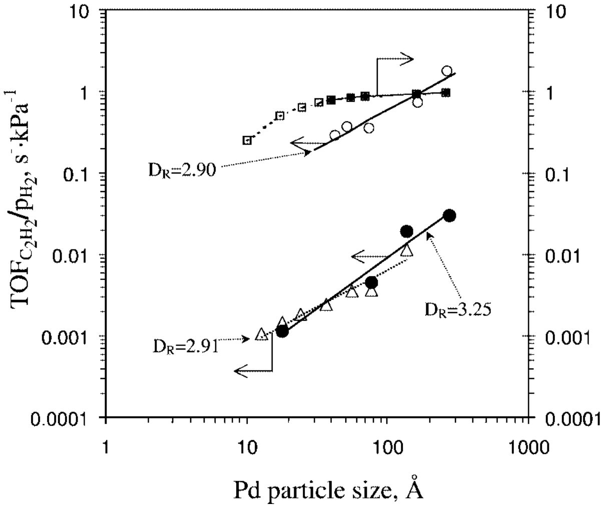


Figure 4. $\mathrm{TOF}_{C_2H_2}/p_{H_2}$ versus Pd particle size: (○) hydrogenation of acetylene on Pd/SiO$_2$ catalysts at $p_{C_2H_2} = 0.1$ kPa, $p_{C_2H_4} = 39.4 \pm 1.0$ kPa and $p_{H_2} = 0.22$–0.71 kPa, $T = 353 \pm 0.2$ K; (△) hydrogenation of acetylene on Pd/Al$_2$O$_3$ catalysts at $p_{C_2H_2} = 10.9$ kPa, $p_{C_2H_4} = 913$ kPa and $p_{H_2} = 456$ kPa, $T = 298$ K (recalculated results of Gigola et al. [6]); (●) Pd/Al$_2$O$_3$ catalysts at $p_{C_2H_2} = 12.8$ kPa, $p_{C_2H_4} = 1098$ kPa and $p_{H_2} = 243$ kPa, $T = 288$ K (recalculated results of Andúriz et al. [7]); (□, ■) fraction of face Pd atoms located in the exposed Pd (100) and (111) faces of crystallites calculated by using van Hardeveld and Hartog's model [30] for fcc cubo-octahedra ((■) denote the data calculated for the present experimental range of d in the kinetic studies on hydrogenation of acetylene on Pd/SiO$_2$ catalysts), n_s denotes the number of Pd atoms on the surface of fcc cubo-octahedra, and n_{pl} denotes the number of Pd atoms on the surface of the exposed Pd (100) and (111) faces of fcc cubo-octahedra.

Another important geometric factor which may have a large influence on the structure sensitivity of the reaction, is the ensemble size effect [31–36]. Obviously for sufficiently small d when the area of the faces of palladium crystallites is not much larger than that of the ensemble of the atoms active in the reaction, the number of the ensembles per unit metal area increases with d. According to the statistical models [33–36], the effect is more dramatic for large ensembles and at high coverages of the active sites by poisons. The carbonaceous deposits can behave as poisons, which block the reactants adsorption sites [19,20,29,32,37]. Then, the ensemble effect can be considered responsible for the higher experimental D_R values than the value calculated on the assumption that only Pd atoms lying in the faces of the crystallites are active. In the present kinetic model of hydrogenation of acetylene–ethylene mixtures, the active A and E sites are assumed to be composed of at least three adsorption sites surrounded by carbonaceous deposits [19,20]. Thus, the active sites involve the relatively large ensembles of palladium surface atoms. Taking into account that the coverage of the surface by carbonaceous deposits is very high, it may be suggested that the ensemble effect plays an important role in the structure sensitivity of the reaction. Consequently, the observed large D_R values for acetylene and ethylene hydrogenation are suggested to originate from both: (i) the statistics of the face atoms in Pd crystallites, and (ii) the surface-site statistics in the crystallite faces carrying carbonaceous deposits. The experimental D_R values for the acetylene hydrogenation and for ethylene hydrogenation are similar (tables 3 and 4). It is in accordance with the assumption that the A and E active sites are similar in nature (the regions of palladium surface between the carbonaceous deposits). This also explains why the overall selectivity is almost independent of d over a very wide range of d (see equation (11) and figure 2(B)), whereas the TOF for acetylene and ethylene hydrogenation strongly increases as d is increased.

4. Conclusions

The antipathetic structure sensitivity of acetylene and ethylene hydrogenation over the Pd/SiO$_2$ catalysts is observed over a very wide range of Pd particle size ($d = 42$–262 Å). This phenomenon is due to the geometric effect. For all the three main reactions the average surface concentration of active sites and, consequently, the frequency factors of the rate constants increase as d is increased, following the scaling law [27,28]. At the same time, d has no influence on the mechanism of the reaction and on the adsorption strengths of acetylene and ethylene molecules. The mechanism of the reactions observed on the Pd/SiO$_2$ catalysts is similar to that observed previously for the Pd/α-Al$_2$O$_3$ catalysts [19,20,25]: the carbonaceous deposits produce specific types of sites for acetylene and ethylene hydrogenation (sites A and E) and act to transmit hydrogen atoms to the reacting molecules of acetylene. The contribution of acetylene hydrogenation proceeding via hydrogen transfer from the deposits increases as $p_{C_2H_2}$ is increased. The large values of the reaction dimensions for acetylene and ethylene hydrogenation ($D_R^A = 2.899 \pm 0.046$ and $D_R^E = 2.987 \pm 0.063$) originate from both (i) the statistics of the face atoms in Pd crystallites, (ii) the surface-site statistics on the crystallite faces covered by carbonaceous deposits. The similar D_R values for the acetylene and ethylene hydrogenation are consistent with the assumption that the A and E active sites are similar in nature (the surface palladium regions between carbonaceous deposits). This also explains why the overall selectivity is almost independent of d over the range 42–262 Å. A general kinetic model of hydrogenation of acetylene–ethylene mixtures on Pd/SiO$_2$ catalysts has been developed. This model describes the effects of d and partial pressures of reactants on the activity and selectivity of the catalysts.

Acknowledgement

The author thanks Professor Michel Che (Laboratoire de Réactivité de Surface et Structure, Université P. et M. Curie, Paris) for kindly supplying the sample of the SE$_{2.6}$ catalyst.

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