Surface chemistry and catalysis studies on the palladium–boron system in the semihydrogenation of alkynes

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A new, supported Pd–B/SiO_2 catalyst characterized by its high bond- and stereo-selectivity in semihydrogenation of –C≡C– triple bond is reported. To elucidate its mode of action a model system, Pd(111)–B, was exposed to H_2, C_2H_2 or C_2H_4 and then investigated by means of AES–LEED–TDS methods. We conclude that there is a geometric blockage of Pd active surface sites by boron adspecies, that their total number diminishes and that the distribution of particular surface ensembles changes.

Keywords: Pd–B modified catalysts; alkynes semihydrogenation; selectivity; Pd(111)–B surface reactivity; AES; TDS; hydrogen sorption; ethyne adspecies

1. Introduction

There is considerable interest in exploring the function of additives to catalysts, called "modifiers". When introduced onto a catalyst surface, they effect the selectivity in a given complex reaction toward the preferential formation of a particular, desired product. Among those modified systems there are transition metals (e.g. Fe, Co, Ni, Pd, etc.) "borided" as a result of reduction of their salts by a sodium borohydride solution [1]. Several accounts review present knowledge on those modified catalysts, particularly as what concerns their utility in selective hydrogenation reactions, in methanation or Fischer–Tropsch syntheses [2–6].

In the present study a modifying action of boron has been investigated in a recently proposed Pd–B/SiO_2 supported catalytic system, favouring the semihydrogenation of a triple bond –C≡C– to the double one $(Z){>}C{\equiv}C{<}$, similar to the Pd–Pb alloy catalyst reported earlier [7,8]. The same experimental procedures as outlined in refs. [7,8] were used in that case. The parallel investigations concerned a similar (but model) system Pd(111)–B, whose well-determined surface aimed to reveal eventually its ability to template the chemisorptive properties and in consequence to help in the interpretation of its catalytically selective preferences.

2. Experimental

2.1. SEMIHYDROGENATION OF CARBON–CARBON TRIPLE BONDS ON A Pd–B/SiO_2 CATALYST

The 5% Pd–O, 7% B/SiO_2 (wt%) catalysts were produced according to the procedure [9] based on that used earlier in Pd–B black catalysts preparation [3]. The palladium chloride solution impregnating a portion of silica-gel (Porasil D, 80–100 mesh) underwent reduction with an aqueous solution of sodium borohydride, at ambient temperature, upon vigorous stirring for 30 min and washing with water and methanol, before drying over potassium hydroxide. After 24 h the catalyst was introduced into respective reactant mixtures: (1) 2-butyne vapour and hydrogen, or (2) 12-tetrahydropyranyloxy-3-tetradecyne and hydrogen (in methanol solution). In both cases a triple carbon–carbon bond is to be converted into a double one, with an eventual choice of a stereo-selective catalytic reactivity toward one of olefinic products: (Z)- or (E)-isomer. The routine performance of the above hydrogenation reactions catalysed by Pd–B/SiO_2, i.e. reactants, reactor systems, reaction conditions, analyses of reaction mixtures were described in detail previously [7,8].

2.2. SURFACE REACTIVITY OF A MODEL CATALYTIC SYSTEM Pd(111)–B IN RESPECT OF H_2, C_2H_2 AND C_2H_4

AES, LEED and TDS experiments were performed in a conventional UHV system (base pressure in the range of 1×10^{-7} Pa) equipped with a three-grid LEED–AES optics (VG) and quadrupole mass spectrometer (QMS 7B, VG). The preparation of the model Pd(111) catalyst sample, its mounting and cleaning were described in detail previously [10]. The temperature was monitored with a NiCr–Ni thermocouple spot welded to the back of the sample.

High-purity hydrogen, ethyne and ethene were introduced from glass bulbs through leak valves. The adsorption of each gas separately on the model catalyst surface at 300 K was performed under the pressure of 1×10^{-6} Pa. During the thermal desorption process the heating rate, β, of the sample was about 31 K/s. Desorption products were analyzed by a quadrupole mass spectrometer. During a programmed increase of temperature hydrogen was desorbing into a well evacuated UHV chamber ($p < 2 \times 10^{-7}$ Pa); molecules of hydrocarbons: $m/e = 26$ and $m/e = 28$ into a low pressure flow of respective gases admitted gently to the UHV chamber ($p = 1 \times 10^{-6}$ Pa).

Boron-covered surfaces of the model Pd(111) catalyst were prepared by adsorption and decomposition of a molecular precursor of boron: B_2H_6 (1% diborane in argon) at 300 K. (Separate publication will be devoted to relations on the interaction of diborane with Pd(111) and the high-temperature behaviour of adsorbed boron.) The boron surface concentration X_B, expressed as atomic ratio n_B/n_{Pd}, was calculated on the basis of the algorithm [11] for quantitative AES analysis of binary alloy surfaces. Such a calibration procedure was adopted in the present paper because of the near coincidence of the boron KLL (179 eV) and the palladium MNN (192 eV) Auger signals and the lack of a characteristic LEED pattern of the Pd(111)–B surface. The calculations were based on the assumption of the uniformity of boron concentration within the depth of the AES analysis. During the experimental procedure the intensity of palladium MNN (330 eV) Auger signal was recorded for clean, $H^0_{Pd}(330)$ or precovered with boron Pd(111) surface, $H^B_{Pd}(330)$. The method used for the calculation of boron surface concentration was reported in detail in ref. [11].

3. Results and discussion

3.1. SELECTIVITY OF THE Pd–B/SiO_2 CATALYSTS IN THE SEMIHYDROGENATION OF ALKYNES

The kinetics of the gas phase hydrogenation of 2-butyne and the liquid phase hydrogenation of 12-tetrahydropyranyloxy-3-tetradecyne on the Pd–B/SiO_2 catalysts are shown in figs. 1a and 1b. The high bond- and stereo-selectivity toward the respective (Z)-alkene formation in both catalytic reactions is observed (fig. 1). In the case of 2-butyne hydrogenation (fig. 1a) the selectivity toward (Z)-2-butene formation is 96.7% at 99.99% of alkyne total conversion, while in the second case the selectivity toward 12-tetrahydropyranyloxy-3-tetradecyne semihydrogenation (fig. 1b) amounts to 99.9% of (Z)-olefinic product at the same final concentration of alkyne in the reacting mixture. It should be stressed that in the latter case the selectivity of the semihydrogenation of a –C≡C– bond toward a (Z) C≡C bond keeps its high value, even when the last traces of the alkyne have already vanished. Such a behaviour of the modified catalytic system, demonstrating its ultimate selectivity, is a particularly important requirement in the reaction studied. The product is involved in a technology of insect sex pheromones and it must guarantee an extremely high dominance of an olefin in desired stereoisomeric form.

3.2. INTERACTION OF H_2, C_2H_2 AND C_2H_4 WITH THE SURFACE OF THE MODEL Pd(111)–B SINGLE CRYSTAL CATALYSTS

The effect of boron on the reactivity of Pd(111) surface in the hydrogenation of ethyne and ethene has been studied [12]. Adsorption (at 300 K) of respective

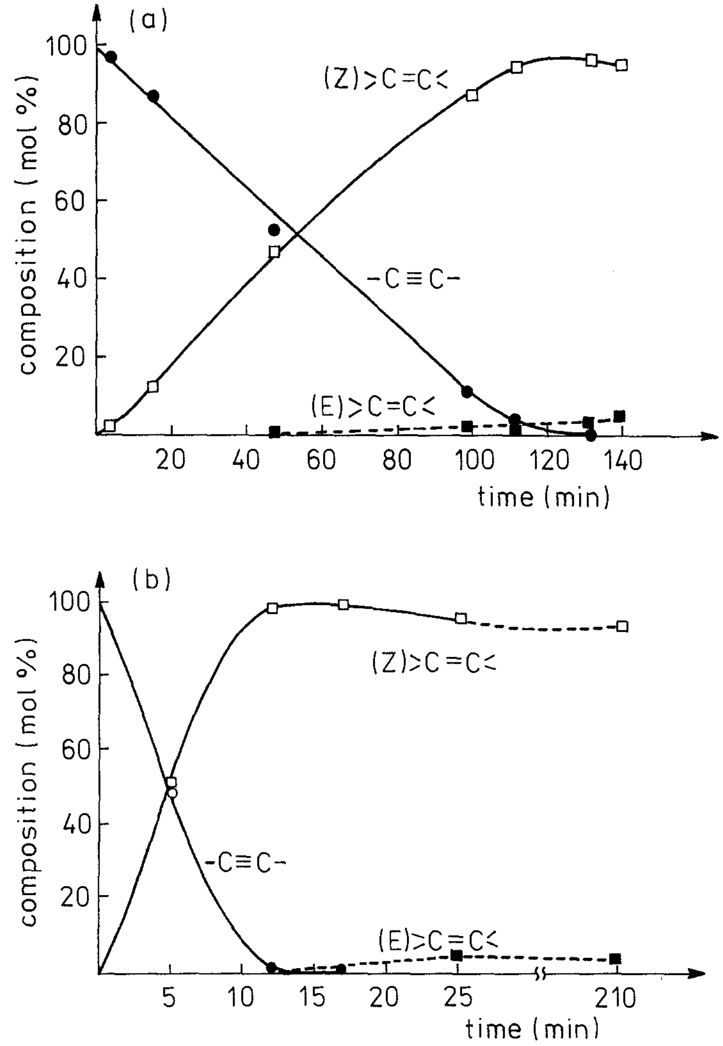

Fig. 1. Change of hydrocarbon concentration with time during the hydrogenation reaction on the Pd–B/SiO_2 catalysts. (a) Hydrogenation of 2-butyne: $T = 293$ K, mass of catalyst = 0.0033 g, initial ratio C_4H_6/H_2 (vol%/vol%) = 44.4/55.6; (b) hydrogenation of 12-tetrahydropyranyloxy-3-tetradecyne (0.108 g in 10 ml CH_3OH): $T = 293$ K, mass of catalyst = 0.03 g.

reactants on Pd(111) surface, clean or precovered with boron of controlled surface concentration, was followed by thermal desorption (TDS). The relevant results are displayed in fig. 2. The thermal desorption spectrum of hydrogen from clean Pd(111) surface (curve 1 in fig. 2) consists of two peaks. The first sharp peak, denoted as β in the literature [13], with $T_m \approx 370$ K, has been assigned to recombination of hydrogen adatoms (H_{ad}) and subsequent desorption of molecular hydrogen. The second broad signal, detected between 470 and

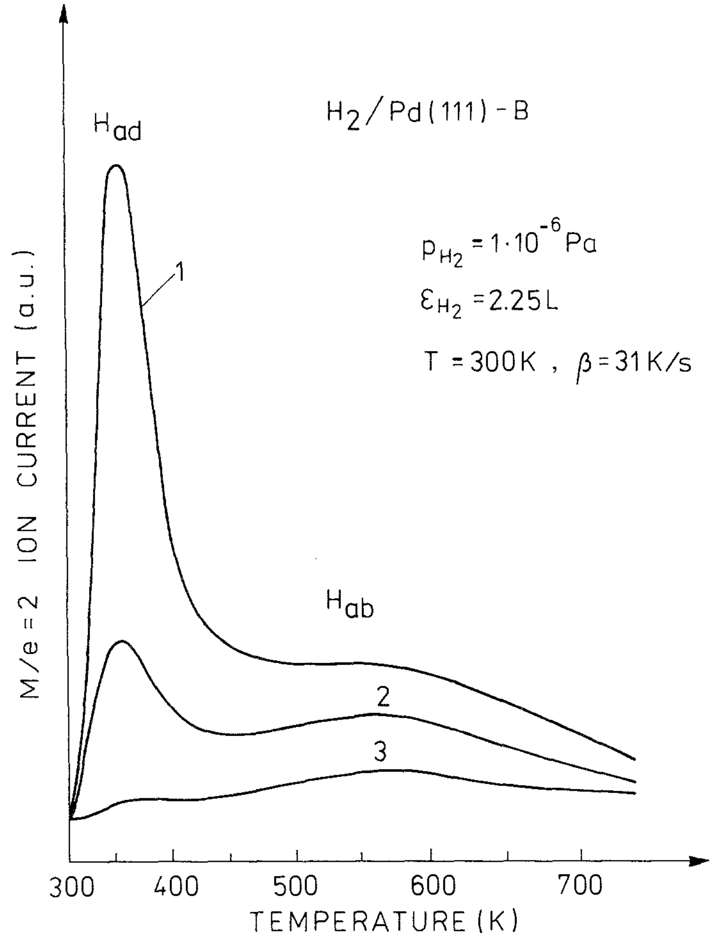

Fig. 2. TD spectra of hydrogen ($m/e = 2$ amu) from Pd(111) and Pd(111)–B surfaces; H_2 sorption at 300 K: (1) clean Pd(111); (2) $X_B = 0.05$; (3) $X_B = 0.16$.

750 K, is ascribable to desorption of hydrogen from the palladium bulk phase (H_{ab}). These results are consistent with the previously reported behaviour of H_2 presorbed onto the clean Pd(111) surface [13/14]. The presence of boron on the Pd(111) surface does not change either the shape of the desorption spectra or the position of the desorption peaks (curves 2 and 3 in fig. 2). This indicates, that the surface binding energy of adsorbed hydrogen with palladium surface atoms has not been distinctly influenced by the presence of boron. The increase of boron surface concentration results in the rapid decrease of the hydrogen sorption as it is seen in fig. 2.

The Pd(111) surface precovered with C_2H_2 (or C_2H_4), adsorbed at moderate temperature ($T \geqslant 300$ K), reveals in the TD spectra the $m/e = 2$ signal. Two maxima of hydrogen desorption in the TDS were observed in the present study: at $T_m \approx 500$ K and within the range of $T_m = 580$–750 K. The distinct first one may be related to vinylidene $/{\equiv}C{\equiv}CH_2/_{ad}$ losing one H atom; then the broad T_m shoulder is ascribable to acetylide $/{-}C{\equiv}CH/_{ad}$ dehydrogenation followed by the gradual final graphitisation of the carbonaceous overlayer. It is generally acknowledged that those effects, progressing with temperature, indicate the scission of C–H bonds in hydrocarbon adspecies. Those adspecies present in the carbonaceous overlayer have been identified as vinylidene or acetylide admolecules (additionally also ethylidyne, $/{=}C{-}CH_3/_{ad}$, when hydrogen is present in a reactant mixture). The identification of those hydrogen deficient carbonaceous adspecies has been proved by surface analyses (HREELS, XPS, UPS, ARUPS and TDS) recorded after ethyne or ethene adsorption on transition metal surfaces such as nickel, ruthenium, rhodium, palladium, platinum, etc. [15].

The Pd(111)–B samples, with variable boron content, precovered with carbonaceous products of C_2H_2 (or C_2H_4) adsorption at $T \approx 300$ K were submitted to the same thermal desorption procedure as above. The TDS demonstrated identical character as the Pd(111) sample, i.e. two hydrogen desorption peaks similarly situated in the spectra. A unique difference consisted in a much lower quantity of desorbing hydrogen, still diminishing with an increase of boron surface concentration on palladium, X_B. These results are ascribable to a lower degree of metal coverage with hydrocarbon adsorbate.

A number of recent studies have shown the absence of molecularly adsorbed C_2H_2 on metals (e.g. Ni, Ru, Rh, Pd, etc.) surfaces at $T \geqslant 300$ K [15]. C_2H_2 does not appear in the respective TD spectra either. Contrary to this previous information and to what was occurring on clean Pd(111) surface in the present study, molecular ethyne ($m/e = 26$) was observed to desorb from the "borided" Pd(111)–B surface. The respective T_m amounts the value of about 365 K, independent on boron concentration, X_B. The amount of desorbing C_2H_2 molecules is influenced by the X_B values, demonstrating a clear maximum on the curve in fig. 3.

Hydrogen, ethyne and ethene adsorption and surface reactivity at the interface Pd(111)–B/H_2, C_2H_2 or C_2H_4 have been studied in detail. The results will be reported separately.

4. Conclusions

Studies on semihydrogenation of chosen alkynes, catalysed by the Pd–B/SiO_2, were performed in parallel with the analysis of surface reactivity of a model Pd(111)–B catalyst in respect of the reactants of ethyne consecutive hydrogenation.

The following conclusions may be drawn:

(1) The "real" Pd–B/SiO_2 catalyst revealed its excellent bond- and stereoselectivity in semihydrogenation of the studied alkynes toward the respective (Z)-alkene products.

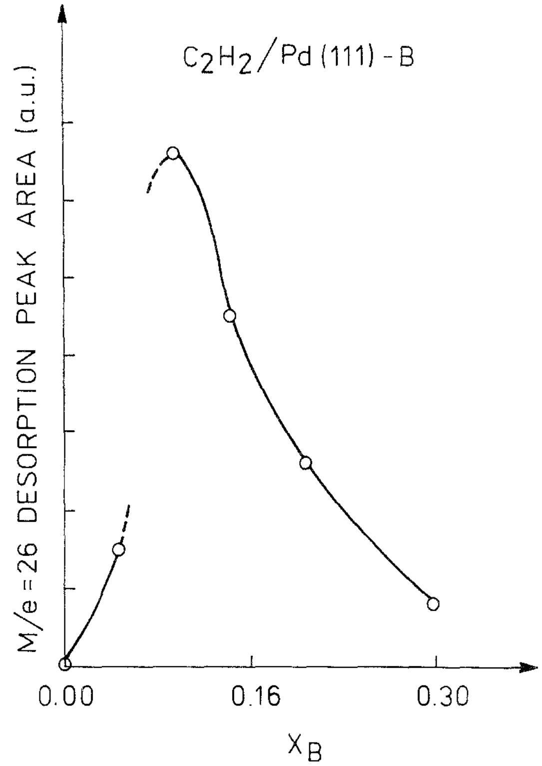

Fig. 3. Relationship of the TD peak area ($m/e = 26$ amu), representing the amount of molecularly adsorbed ethyne, as a function of boron surface concentration X_B.

(2) The boron adspecies are partly blocking active surface sites of palladium, necessary for H_2, C_2H_2 or C_2H_4 chemisorption. In consequence: (i) the surface coverage with reactant intermediates diminishes, (ii) the surface tailoring effect, induced by modifier adspecies, favours an abundance of templates, that contain ensembles with a lower number of active sites – two or one, as one can deduce from the LEED pattern displayed in the case of the model Pd(111)–Pb modified system [8], demonstrating a similar behaviour as the Pd(111)–B one.

(3) Studies of the model Pd(111)–B modified catalyst seem to justify the expectation of a decrease of the rate of alkyne total hydrogenation, that favours a relative increase of the rate of its first stage, i.e. alkyne to alkene conversion, thus explaining enhanced selectivity in presence of boron.

References

[1] H.J. Schlesinger, H.C. Brown, H.R. Hoekstra and L.R. Rapp, J. Am. Chem. Soc. 75 (1953) 199;
H.J. Schlesinger, H.B. Brown, A.E. Finholt, J.R. Gilbreath, H.R. Hoekstra and E.K. Hyde, J. Am. Chem. Soc. (1953) 215.

[2] R.C. Wade, D.G. Holah, A.N. Hughes and B.C. Hui, Catal. Rev. Sci. Eng. 14 (1976) 211.

[3] W. Palczewska, M. Cretti-Bujnowska, J. Pielaszek, J. Sobczak and J. Stachurski, in: *Proc. 9th Int. Congress on Catalysis*, Vol. 3, eds. M.J. Phillips and M. Ternan (The Chemical Institute of Canada, Ottawa, 1988) p. 1410.

[4] C.H. Bartholomew and A.H. Uken, Appl. Catal. 4 (1982) 19;
J. Wang and C.H. Bartholomew, in: *Proc. 9th Int. Congress on Catalysis*, Vol. 2, eds. M.J. Phillips and M. Ternan (The Chemical Institute of Canada, Ottawa, 1988) p. 813;
J. Wang and C.H. Bartholomew, Appl. Catal. 62 (1990) 221.

[5] Y.Z. Chen and J. Wu, Appl. Catal. 78 (1991) 185.

[6] V.M. Deshpande, W.R. Patterson and C.S. Narasiman, J. Catal. 121 (1990) 165, 174.

[7] W. Palczewska, I. Ratajczykowa, I. Szymerska and M. Krawczyk, in: *Proc. 8th Int. Congress on Catalysis*, Vol. 4 (Verlag-Chemie, Weinheim, 1984) p. 173.

[8] J. Sobczak, T. Bolesławska, M. Pawłowska and W. Palczewska, in: *Heterogeneous Catalysis and Fine Chemicals*, Studies in Surface Science and Catalysis, Vol. 41, eds. M. Guisent, J. Barrault, C. Bouchoule, D. Duprez, C. Montassier and G. Pérot (Elsevier, Amsterdam, 1988) p. 197.

[9] W. Palczewska, J. Sobczak and M. Cretti-Bujnowska, Polish Patent appl. P-288 938 (1991).

[10] I. Ratajczykowa, J. Vac. Sci. Technol. A1 (1983) 1512.

[11] A. Jabłoński, Surf. Interface Anal. 4 (1982) 135;
A. Jabłoński, M. Krawczyk and B. Lesiak, J. Electron Spectry. Rel. Phenom. 46 (1988) 131.

[12] M. Krawczyk, PhD Thesis, Dept. of Catal. on Metals, Inst. of Phys. Chem., Pol. Acad. Sci., Warsaw (1992).

[13] G.E. Gdowski, T.E. Felter and R.H. Stulen, Surf. Sci. 181 (1987) L147.

[14] I. Ratajczykowa, Surf. Sci. 172 (1986) 691.

[15] P.A.P. Nascente, M.A. Van Hove and G. Somorjai, Surf. Sci. 253 (1991) 167.