



n-Hexane Hydrogenolysis Behavior of Alumina-Supported Palladium–Platinum Alloys

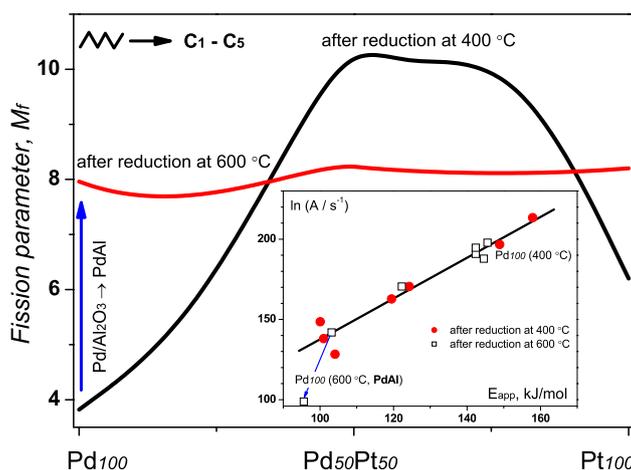
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Received: 30 April 2019 / Accepted: 25 June 2019 / Published online: 6 July 2019
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Abstract

The behavior of alumina-supported palladium–platinum catalysts in the reaction of n-hexane hydrogenolysis was analyzed. The monometallic Pt/Al₂O₃ catalyst showed much higher activity than the rest of catalysts. The relationship between the catalytic activity of Pd–Pt/Al₂O₃ catalysts and bulk Pd–Pt composition matched the accepted relation between the surface composition and bulk composition of Pd–Pt, confirming a high surface enrichment in palladium. A linear relation between the apparent activation energy and preexponential factor (compensation effect) suggests that the reaction mechanism is similar for all Pd–Pt catalysts. However, after very high temperature of catalyst reduction (at 600 °C), the behavior of monometallic Pd/Al₂O₃ catalyst exhibited a considerable departure from the compensation plot, and drastic variations in C₁–C₅ products distribution. Such big changes are rationalized by assuming the transformation of Pd/Al₂O₃ into Pd–Al alloy, occurring at very high temperature of reduction. Product distribution of n-hexane hydrogenolysis for Pt/Al₂O₃ differs from that of Pd/Al₂O₃, showing more internal bond splitting than a terminal demethylation. However, bimetallic Pd–Pt/Al₂O₃ catalysts showed even more ‘internal bond splitting’ character than the Pt/Al₂O₃. Reasons for this synergism and changes in the behavior of Pd/Al₂O₃ catalysts are analyzed in terms of an electronic interaction between metals and alumina support.

Graphic Abstract



Keywords Pd–Pt/Al₂O₃ · n-Hexane hydrogenolysis · Effect of alloying · Effect of catalyst reduction temperature · Compensation effect · Hydrogenolysis pattern

Electronic supplementary material The online version of this article (<https://doi.org/10.1007/s10562-019-02887-4>) contains supplementary material, which is available to authorized users.

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1 Introduction

Technological superiority of several Pt-based alloy catalysts in naphtha reforming, e.g., Pt–Sn, Pt–Ru, Pt–Ir, Pt–Rh resulted in a large number of patents, source papers, reviews, and monographs (e.g. [1]). Introduction of a second metal to platinum often leads to a higher catalytic activity, better selectivity toward desired products (e.g. isomeric or aromatic compounds) and an increased catalyst's life-time. More recent attention was focused on Pt–Pd alloy catalysts which showed a superior sulfur tolerance, compared to the behavior of monometallic Pt catalysts, supported on acidic supports such as zeolite H-Beta [2]. Recently, in a post-conference paper we reported results on the catalytic behavior of Pd–Pt/Al₂O₃ catalysts in the reaction of n-hexane conversion [3]. Our main attention was turned to the problems how to prepare well mixed Pd–Pt catalysts and how the conditions of catalyst pretreatment influence the alkane isomerization behavior. It appeared that a simple incipient impregnation of alumina with toluene solutions of acetylacetonates of palladium and platinum yields reasonably well alloyed Pd–Pt/Al₂O₃ catalysts, whereas a similar preparation technique with the use of respective metal chlorides results in poorly mixed bimetallic catalysts and chloride retention in the alumina support. It appears that the interaction of both metal acetylacetonates takes place already in a toluene solution [4], similarly to the situation with Pd–Cu acetylacetonates [5]. It leads to the situation that upon impregnation, palladium and platinum are deposited in a close vicinity to each other. The degree of Pd–Pt alloy homogeneity had a significant effect on the relations of catalytic activities and product selectivities with Pd–Pt alloy composition. At that time the hydrogenolysis behavior was not practically considered. It was so because in contrast to fluid catalytic cracking on zeolites, the hydrogenolysis of alkanes by metals is not of great technological importance, although the structure sensitivity often found in this reaction had in the past great usefulness in showing how the structure of the surface of small metal (and alloy) particles depended on their size. In addition, a common knowledge that among the most important catalytic metals, palladium and platinum exhibit the lowest activity in alkane hydrogenolysis [6–9] restricted our interest mainly to the isomerization [3]. However, shortly thereafter we realized that it would also be interesting to consider the hydrogenolysis behavior of Pd–Pt/Al₂O₃ catalysts. Irrespective of the fact that both metals showed indeed quite low catalytic activity in alkane hydrogenolysis, they produced different patterns of hydrogenolysis products. On palladium, the major hydrogenolysis reaction is demethylation, whereas on platinum, apart from demethylation, secondary–secondary C–C bond

ruptures become important. [9–11]. It turned out rather unexpectedly that the introduction of palladium (i.e. the metal on which mainly runs demethylation) to platinum enhances the propensity for splitting internal C–C bonds. This “synergistic effect” and the effect of high temperature reduction on the hydrogenolysis behavior of Pd–Pt/Al₂O₃ catalysts are reported and discussed in this paper.

2 Experimental

Catalyst preparation and characterization (TPR, H₂ chemisorption, XRD and TEM) were described in our previous report [3]. Briefly, 1 wt% of Pd–Pt/ γ -alumina (Sasol Puralox Scca, 150–200 mesh, surface area ~ 200 m²/g) catalysts were prepared by an incipient wetness impregnation of alumina with a mixture Pd and Pt bis-acetylacetonate precursors (Pd(acac)₂ and Pt(acac)₂ from Sigma-Aldrich, 99%) dissolved in toluene (analytical reagent from Chempur, Piekary Śląskie, Poland. In further text, the catalysts are designed as Pd_XPt_Y, where X and Y stand for atomic percentages of Pd and Pt in the metal phase.

Catalytic activity measurements were described in our previous report [3]. Briefly, the hydroconversion of n-hexane was conducted in a continuous-flow reaction glass system under atmospheric pressure. The partial pressure of n-hexane was 6.0 kPa, resulting in H₂-to-hexane ratio ~ 16:1.

Turnover frequencies (TOFs) were calculated on the basis of the metal fraction exposed measured by pulse H₂ chemisorption [3]. Product selectivities were calculated as the carbon percentage of n-hexane consumed in the formation of a designated product.

3 Results and Discussion

Characterization of 1 wt% Pd–Pt/Al₂O₃ catalysts subjected to different reduction conditions was described elsewhere [3]. Table 1 exemplifies the most important results concerning metal dispersion data. The catalysts showed rather good metal dispersions, with metal particle sizes ca. 2 nm, as measured by TEM, and small decrease in metal dispersion produced by catalyst reduction at higher temperatures (up to 600 °C). STEM-EDX data showed a relatively good degree of Pd–Pt alloying. Reasonable information about the composition of Pd–Pt alloy phases was assessed from catalytic data and was supported by STEM-EDX results. The relation between TOF and the Pd–Pt bulk composition exhibited a concave shape, characterized by a rather sharp decrease of TOF for Pt-rich alloys, and much milder changes for the rest of Pd–Pt alloys which showed very low catalytic activity. This relation, implying a high surface enrichment in palladium, matches the accepted relationship between the surface

Table 1 Metal dispersion in 1 wt% Pd–Pt/Al₂O₃ catalysts after reduction at 400 °C for 17 h

Catalyst ^a	H/(Pd + Pt) ^b	d (nm) ^c
Pd100	0.28	4.0 (2.5 ^d)
Pd80Pt20	0.234	4.8 (2.6 ^d)
Pd60Pt40	0.296	3.8 (2.3 ^d)
Pd50Pt50	0.334	3.4 (2.4 ^d)
Pd40Pt60	0.351	3.2 (2.0 ^d)
Pd20Pt80	0.395	2.8 (1.5 ^d)
Pt100	0.445	2.5 (1.3 ^d)

^aIn the notation PdXPtY, X and Y denote atomic percentages of Pd and Pt, X + Y = 100 (%)

^bMetal dispersion from hydrogen chemisorption (pulse method)

^cBased on the relations: $d_{Pd}(\text{nm}) = 1.12/(H/Pd)$, from Ichikawa et al. [12], and $d_{Pt} = 1.13/(H/Pt)$, from Rachmady and Vannice [13]

^dNumbers in the brackets show the results of TEM measurements

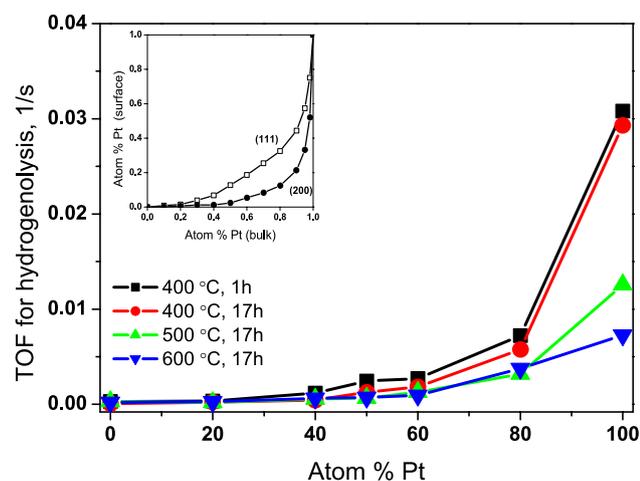


Fig. 1 Catalytic activity of 1 wt% Pd–Pt/Al₂O₃ in the reaction of n-hexane hydrogenolysis after different conditions of catalyst's reduction, indicated in the graph. Reaction temperature 291 °C. Inset: the relation between surface and bulk composition of Pd–Pt alloys adapted from Rousset et al. [14]

and bulk compositions of Pd–Pt alloys [14]. Pd100/Al₂O₃ showed higher than Pt100/Al₂O₃ selectivity for isomerization, especially after reduction at higher temperatures, at 500 and 600 °C. On alloying with Pt, the selectivity for isomerization was very high for nearly all bimetallic catalysts and showed a small synergistic effect for 20 at.% Pt [3]. A similar synergy was found in neopentane isomerization carried out on silica-supported Pd–Pt alloys [15, 16].

All basic experimental data covering the catalytic behavior of Pd–Pt/Al₂O₃ catalysts in the reaction of n-hexane hydrogenolysis are collected in the Electronic Supporting Material (Tables 1–8 (ESM)), whereas the most important correlations will be presented graphically (Figs. 1, 2, 3,

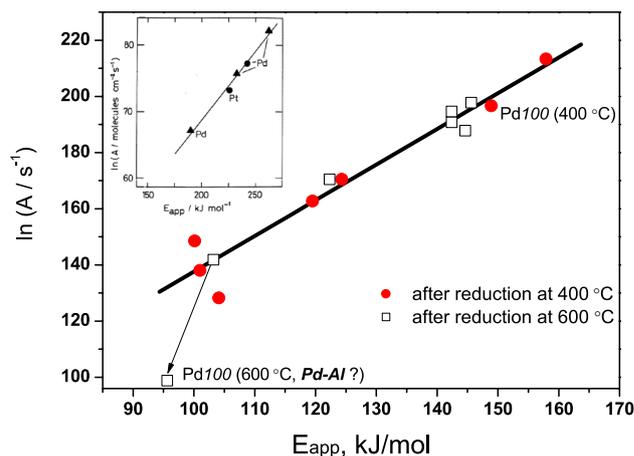


Fig. 2 Compensation plot for the hydrogenolysis of n-hexane on 1 wt% Pd–Pt/Al₂O₃ catalysts. Red circles—catalysts reduced at 400 °C for 1 h, open squares—catalysts reduced at 600 °C for 17 h. Inset: compensation plot for ethane hydrogenolysis on silica-supported Pt and Pd catalysts adapted from Bond [18]

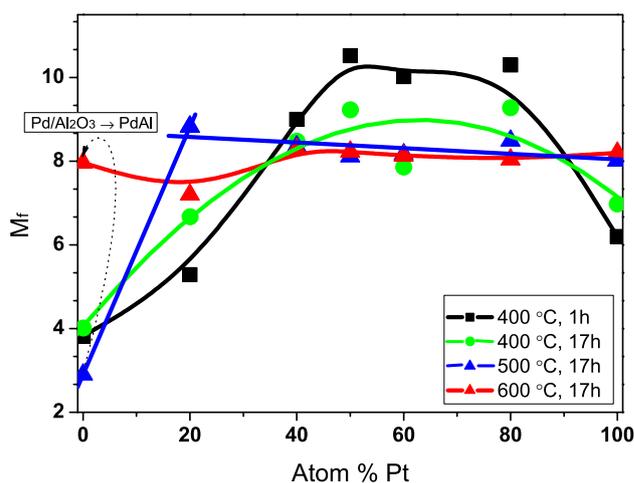
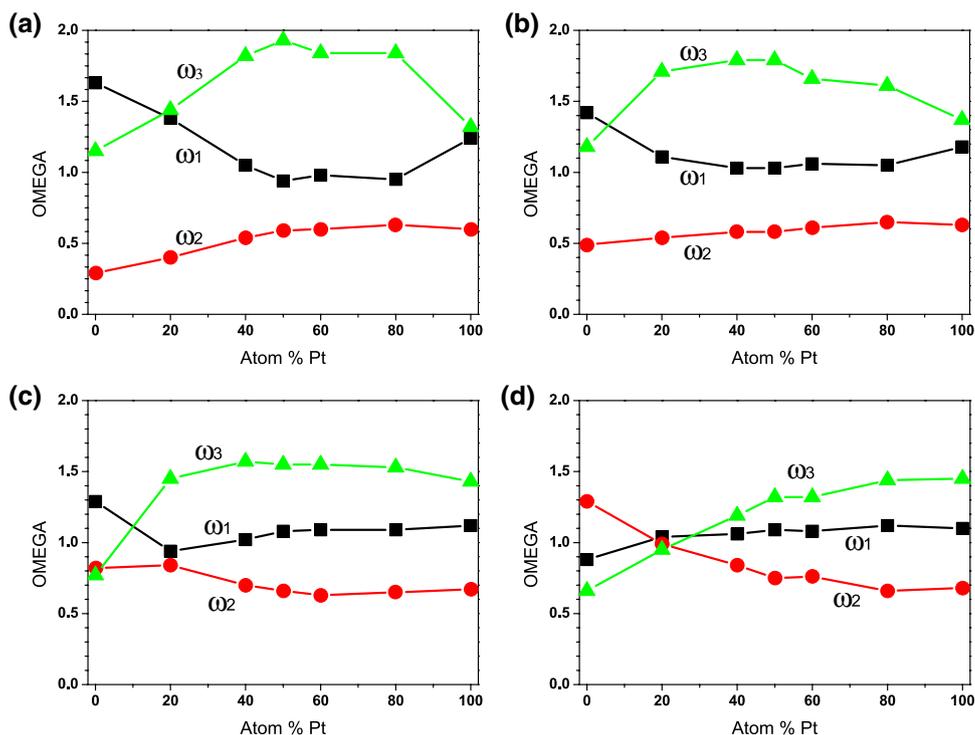


Fig. 3 Variations of M_f parameter with Pd–Pt alloy composition. n-Hexane conversion at 291 °C

4). As mentioned in our previous publication [3], the main reactions occurring during n-hexane hydroconversion at the reaction temperatures ≤ 291 °C were hydrogenolysis and isomerization (dominant reaction). Since the variations in isomerization selectivity were previously discussed, it would be now rather impractical to spend time on discussion of changes in the overall selectivity for hydrogenolysis. Negligible amounts of isobutane and isopentane in products (Tables 5–8 (ESM)) allow to treat both reaction pathways (hydrogenolysis and isomerization) as independent and discuss the relationship between the rate of n-hexane hydrogenolysis ($\text{TOF}_{\text{hydrog}}$) and the composition of Pd–Pt alloys. To this aim Fig. 1 collects the relevant data. It is seen that,

Fig. 4 n-Hexane hydrogenolysis pattern expressed in terms of omega factors (defined in text) for 1 wt% Pd–Pt/Al₂O₃ catalysts subjected to different reduction conditions. The effect of nominal bimetal composition on the demethylation/internal splitting ratio, calculated as ($\omega_1/(\omega_2 + \omega_3)$): **a** after reduction at 400 °C for 1 h, **b** after reduction at 400 °C for 17 h, **c** after reduction at 500 °C for 17 h, **d** after reduction at 600 °C for 17 h



irrespective of the catalyst' reduction conditions, Pt100 was much more active than the rest of Pd–Pt/Al₂O₃ catalysts. A concave shape of this relation (Fig. 1) is in agreement with our previous conclusion [3] about a considerable surface enrichment of Pd–Pt alloys in palladium (inset in Fig. 1). This is also in line with Wu et al. [16], who concluded that for neopentane hydroconversion on silica-supported Pd–Pt catalysts, the reaction rates and selectivities were determined predominantly by Pt with little contribution from Pd surface species.

It appeared interesting to search for the relation between $\ln A$ ($A = \text{TOF}_0$) and E_{app} (apparent energy of activation) for differently pretreated Pd–Pt/Al₂O₃ catalysts, the compensation effect which was quite often reported for alkane hydrogenolysis reactions, especially for ethane hydrogenolysis [7, 17]. We were encouraged by the results of Bond [18], who constructed a common compensation plot for the hydrogenolysis of ethane on platinum and palladium catalysts, based on the results of Sinfelt [6], inset in Fig. 2. We used the values of apparent energies of activation, which ranged between 95 and 158 kJ/mol (Tables 1–4, (SM)). It must be recalled that the hydrogenolysis rates measured for Pd-rich, Pd–Pt/Al₂O₃ catalysts were found very low, especially for the lowest temperature of reaction (252 °C, Tables 1–4 (ESM)). Therefore, due to uncertainties in estimating TOF values at this temperature, points in the compensation plot constructed from the experimental data for the Pd–Pt/Al₂O₃ catalysts reduced at 400 °C for 1 h, and at 600 °C for 17 h ($\ln \text{TOF}$ vs. E_{app} , Fig. 2) are somewhat scattered. Nevertheless, two things seem worth mentioning. First, a

common compensation plot for the catalysts of different Pd:Pt ratio suggests that the mechanism of n-hexane hydrogenolysis is generally similar, confirming analogous speculations based on the common compensation plot for silica-supported Pt and Pd catalysts shown in the inset in Fig. 2). Second, the departure of one experimental point (for Pd reduced at 600 °C) for the compensation plot indicates that the Pd100/Al₂O₃ experiences big changes after reduction at very high temperature. Our recent work [19] showed that palladium interacts with the alumina support and transforms, even if not fully, into a Pd–Al alloy.

As far as the catalytic characteristics mentioned above are not unexpected in the light of our previous findings, variations in the “hydrogenolysis pattern”, i.e. distribution of hydrogenolysis products, affected by changes in the composition of a catalytically active phase (Pd–Pt) and catalyst's pretreatment, are far more interesting.

Primary analysis of hydrogenolysis products of n-hexane hydroconversion established that the fragmentation factor, ζ , which characterizes the depth of hydrogenolysis as the number of fragment molecules ($i < n$) per molecule of C_nH_{2n+2} alkane split up [10]:

$$\zeta = \frac{\sum_{i=1}^{n-1} C_i}{\sum_{i=1}^{n-1} \left(\frac{i}{n}\right) C_i}$$

was for all Pd–Pt/Al₂O₃ samples 2.059 ± 0.102 (standard deviation), for 291 °C, i.e. the highest reaction temperature,

in consistency with the single bond splitting characteristics of monometallic palladium and platinum catalysts [9, 10]. This result obtained at a low conversion of n-hexane (<5%, in most cases <2%) simplifies further discussion on the effect of Pd–Pt alloy composition on the hydrogenolysis pattern because the contribution of secondary products is insignificant.

As mentioned in the Introduction, palladium and platinum show different hydrogenolysis patterns. On palladium the major hydrogenolysis reaction is terminal demethylation, whereas for platinum, apart from demethylation, the secondary–secondary C–C bond rupture becomes important (10,11,20). A ‘fission parameter’ M_f appears a good measure for treating differences in a quantitative way [21]:

$$M_f = \frac{\sum_{i=2}^{n-1} C_i(n-i)}{C_1}$$

Its value is one for terminal demethylation, while $M_f < 1$ with multiple and $M_f > 1$ with random (so also with internal) splitting. Although this parameter is influenced by reaction conditions (e.g. reaction temperature, H_2 -to-alkane pressure ratio), much higher than in the case of palladium, values of M_f for platinum catalysts reflect the generally accepted view regarding the difference in the catalytic behavior of both metals. Considering similar reaction conditions, the M_f values for different forms of Pd catalysts were reported as close to 2 [22, 23] whereas M_f for Pt catalysts was usually much higher, often approaching a level of ca. fivefold higher [22, 24].

Figure 3 shows results obtained for n-hexane hydrogenolysis over Pd–Pt/ Al_2O_3 catalysts prerduced at different conditions. For the monometallic catalysts, the effect of reduction temperature is not large: for 1 wt% Pt/ Al_2O_3 M_f changes between 6 and 8, whereas for 1 wt% Pd/ Al_2O_3 , with noticeable exception for the pretreatment at 600 °C, it is between 3 and 4. For the bimetallic samples reduced at 400 °C for 1 h and 17 h one observes a distinct maximum in the M_f for ca. 60 at. % Pt. The increase of the temperature of catalyst reduction “flattens” this maximum, finally leading to the situation where nearly all Pd–Pt catalysts show a similar hydrogenolysis pattern after reduction at 600 °C. It is difficult to suggest specific reasons for this effect, however one possibility would be that highly unsaturated metal sites (like edge atoms) are responsible for internal splitting and plane metal atoms are better for terminal demethylation. Such supposition is in line with the hydrogenolysis behavior of unsupported palladium catalysts (powders [10] and single crystals [23]) which generally show lower values of M_f parameter compared to that exhibited by highly dispersed Pd systems (this work). The decrease of M_f for Pd100 after reduction at 500 °C, from ~4 to ~3 (Fig. 3) confirms our hypothesis,

especially, when we recall recently found observation that Pd nanocrystals for samples reduced at 400 °C for 1 h were irregular in shape and exhibited highly distorted crystal lattice, in the opposition to nanocrystals for the sample reduced at higher temperatures. The latter nanocrystals had near perfect crystallinity and were terminated by the {011} type facets (Fig. 8 in Supplementary Material for [19]). The most remarkable change is observed for the monometallic Pd100/ Al_2O_3 catalyst which shows M_f close to 8, characteristic for platinum catalysts (Fig. 3). Obviously, such change is in sharp conflict with the above interpretation and will be discussed a little later.

A closer look into the hydrogenolysis behavior can be obtained from the so-called reactivity factor (ω), describing the pattern of hydrogenolysis of any C–C bond in n-hexane chain. This factor, defined by Leclercq et al. [25] is expressed as:

$$\omega = \frac{\text{Actual rate of rupture}}{\text{Expected rate of rupture (random fission)}}$$

In the case of n-hexane hydrogenolysis, ω_1 , ω_2 and ω_3 stand for the rupture of $H_3C-C_5H_{11}$, $C_2H_5-C_4H_9$ and $C_3H_7-C_3C_7$ bonds, respectively.

Figure 4 shows respective omega factors for all tested catalysts subjected to hydrogen reduction at different temperatures (a, b, c and d). It is observed that n-hexane hydrogenolysis patterns of the monometallic Pd100/ Al_2O_3 and Pt100/ Al_2O_3 catalysts do not differ from each other, so much as it would be expected from earlier studies [10, 20, 22], where the demethylating character of palladium contrasted with an internal splitting of hexane, characteristic for platinum. For instance, Paál and Tétényi [10] give respective omega values for Pd black catalyst: $\omega_1 = 2.61$, $\omega_2 = 0.3$, and $\omega_3 < 0.05$, clearly indicating a dominance of terminal over internal splitting behavior. We believe that this difference would be due to some interactions between palladium and alumina, generated by a high temperature reduction. Our recent work (Fig. 2 in [19]) shows that the $\omega_1/(\omega_2 + \omega_3)$ ratio, which reflects the importance of demethylation over internal rupture, was gradually diminished with the increase of the temperature of Pd100/ Al_2O_3 reduction. The respective omega values for this catalyst reduced at 300 °C were: $\omega_1 = 1.98$, $\omega_2 = 0.21$ and $\omega_3 = 0.61$, being more closer to the respective values obtained for Pd black [10], indicating a more stronger demethylation character of palladium.

Figure 4a and b show that in line with the results of M_f changes in the omega parameters vs. alloy composition indicate that the “more internal” bond rupture character of platinum is not only retained for a majority of Pd–Pt bimetallic catalysts reduced at 400 °C, but it is even considerably enhanced. The increase of the ω_3 factor results

from an increased amount of propane in hydrogenolysis product, Tables 5 and 6 (ESM). It should be recalled that higher amounts of propane in products of n-hexane conversion over bimetallic Pd–Pt/Al₂O₃ catalysts were also observed by others [26], but that finding was not subjected to discussion. We believe that this synergistic effect would be interpreted by accepting variations in the electronic structure of Pd–Pt alloys. There is evidence that Pt atoms in highly dispersed Pd–Pt alloy catalysts are electron-deficient, due to electron transfer from Pt to Pd [2, 27–29]. Electropositive character of Pt atoms (in Pd–Pt) implies their weaker bonding of such adsorbates like CO. Such conclusion is in line with the results of IR study of CO adsorption on Pd–Pt/SiO₂ catalysts [30] and observation that all adsorbed CO bands were shifted to higher frequencies by about 10 cm⁻¹, compared to the positions of respective CO bands for Pt/SiO₂. The weakening of the CO-metal bond implies also a weakening of the alkane-metal bond. Such parallelism was invoked by Childers et al. [31], who even proposed a linear relationship between the energies of CO and hydrocarbon adsorption in the form: $E_{\text{CO,ads}} = 0.60E_{\text{CH}_3,\text{ads}} - 0.09$ (energies in eV). It appears that the weakening of the alkane-metal bonding would lead to an increased internal rupture of n-hexane at the expense of its terminal demethylation. This may be realized by migration of the metal-hexane bond along the molecule chain. Actually, Sinfelt [7] argued that the carbon–metal double bonds (invoked in a large variety of proposed mechanisms of alkane hydrogenolysis on metals, reviewed by Maire and Garin [32], could shift readily from a terminal carbon atom to an internal one along the alkane chain making use of a variable valency of surface atoms. In our case, such specific pairs of metal atoms would be composed of Pt^{σ+} atoms and zerovalent metal species in Pd–Pt alloy surface. In addition, a weaker, compared to terminal, internal C–C bonds in n-hexane molecule would be subjected to a more preferential splitting ($D_{298}^0 = 368.4 \pm 6.3$ kJ/mol for CH₃C₅H₁₁ versus $D_{298}^0 = 366.1 \pm 3.3$ kJ/mol for C₃H₇–C₃H₇, [33]. Figure 3 (a and b) shows that indeed the ω₃ factor becomes increased at the expense of the ω₁ factor, whereas the ω₂ factor experiences only minor changes. Zimmer et al. observed that the decrease of the hydrogen-to-hexane pressure ratios gradually increased the importance of demethylation over internal splitting on Pt black [34]. At such conditions increasing deposition of carbonaceous species makes the surface of platinum less capable for stronger reactant bonding.

It should be recalled that synergistic effects in alkane hydrogenolysis are not new and were reported in the past. For example, in testing platinum–rhenium single crystal surfaces in the hydrogenolysis of ethane, Godbey et al. [35] found that although the Re(0001) surface was two orders of

magnitude more active than the Pt(111) surface, yet a bimetallic surface of the stoichiometry Re₂Pt was found to be the most active surface for ethane hydrogenolysis—about one order of magnitude more active than the Re(0001) surface. This result suggested that an electronic interaction exists between platinum and rhenium metals that strongly influences the catalytic behavior.

Both changes in M_f and omega factors show that the aforementioned synergistic effect is gradually weakened by increasing the temperature of catalyst's reduction. As far as the temperature of catalyst's reduction has not reached 600 °C, the ω₃ factor for a majority of Pd–Pt catalysts is at the level characteristic of platinum (Fig. 4c). However, the reduction at 600 °C (Fig. 4d) clearly changes the relation between the ω₃ factor and Pd–Pt alloys concentration which now it smoothly decreases with palladium introduction to platinum. The ω₁ factor does not apparently change with Pd–Pt alloy composition. It means that n-hexane demethylation, characteristic for palladium catalysts, is not regained. Instead, one observes the increase of ω₂ with the increase of Pd content. This result appears striking because the rupture of C₂H₅–C₄H₉ bond was never favored in the case of platinum and palladium catalysts. It rather recalls the cracking behavior of acidic catalysts [36]. We believe that such behavior may result from generated Pd–Al₂O₃ interactions, identified with Pd–Al alloying, evidenced in earlier publications [37–39] and recently confirmed by us [19]. DFT calculations of small Pd_nAl_m (n + m ≤ 6) clusters showed that the values of vertical ionization potential are much higher than the values of vertical electron affinity, implying that the bimetallic PdAl clusters easily accept electrons [40]. The conclusion about an electropositive character of PdAl clusters can be drawn from other reports. The results of IR studies of CO adsorbed on Pd/Al₂O₃ catalysts reduced at 600 °C (i.e. supposedly transformed into Pd–Al species) [41] revealed the presence of Pdⁿ⁺ ions. Likewise, Rodriguez [42] argued that Pd atoms supported on Al clusters exhibit a net positive charge. This may be a reason why such PdAl clusters are very selective in alkane isomerization [19], and, in addition, a small part of n-hexane is apparently cracked in the way more characteristic for acidic catalysts [43, 44]. Mixed Pd–Al sites would act as an electron sink (weak Lewis acid) for adsorbed n-hexane, creating electron-deficient species that can rearrange in a manner analogous to carbonium ions.

4 Conclusions

1. In the reaction of n-hexane hydrogenolysis the alumina-supported monometallic platinum catalyst showed much higher activity than Pd/Al₂O₃ and all tested Pd–Pt/Al₂O₃ catalysts. The “concave-shaped” relationship between the catalytic activity of Pd–Pt/Al₂O₃ catalysts and bulk

Pd–Pt composition, is reminiscent of the accepted relation between the surface and bulk compositions.

2. A compensation effect between frequency factor and apparent activation energy suggests that the reaction mechanism is similar for all Pd–Pt catalysts. Departure from the compensation plot for the monometallic Pd/Al₂O₃ catalyst pretreated in hydrogen at 600 °C is not unexpected high temperature reduction (at 600 °C) because such severe reduction conditions result in transformation into Pd–Al bimetallic alloy [19].
3. Very big change in the hydrogenolysis behavior of Pd/Al₂O₃ generated by high temperature reduction is also manifested by variations in the product distribution, expressed by different bond fission parameters.
4. Distribution of n-hexane hydrogenolysis products for the platinum catalyst differs from that of palladium one, showing more internal bond splitting than demethylation. However, alloying platinum with palladium enhances this effect. Reasons for the existence of this synergy are seen in the variations of the electronic structure of platinum alloyed with palladium.

Acknowledgements This work was carried out within Research Project # 2016/21/B/ST4/03686 from the National Science Centre (NCN), Poland.

Compliance with Ethical Standards

Conflict of interest The authors declare no conflict of interest.

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