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# Characterization of supported Pd-Pt catalysts by chemical probes

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## Abstract

The temperature programmed (palladium) hydride decomposition appeared very effective method for diagnosing the extent of alloying in Pd-Pt/$SiO_2$ catalysts. Introduction of Pt to Pd catalysts moves the TPHD peak gradually towards lower temperatures and the shift in hydride decomposition peak is accompanied by a decrease in the amount of released hydrogen. The catalysts prepared the direct redox method showed much better alloy homogeneity than the samples prepared by coimpregnation. The results of probing with other techniques, i.e. catalytic probing with hydrodechlorination of $CCl_2F_2$ and XRD, were in line with TPHD data. The catalytic probing showed the presence of synergistic effect, a clear indication of Pd-Pt mixing. XRD data of post-reaction samples showed carbon incorporation into Pd-rich phase, whereas separate Pt-rich phase did not experience any bulk carbiding.

*Keywords:* Pd-Pt/$SiO_2$ catalysts; Temperature programmed hydride decomposition; Hydrodechlorination of dichlorodifluoromethane; X-ray diffraction; Catalyst carbiding

## 1. Introduction

Supported noble metal catalysts have a long history of interest and, because of their exceptional properties, have been used in many industrial processes for many years. A particular advantage of using precious metal catalysts in supported form is that the support disperses the metal over a greater surface area and reduces thermal degradation (sintering). Palladium as well as platinum is unique among the catalytic metals for its high activity and selectivity for hydrogenation, paraffin hydroisomerization, naphta reforming, hydrodechlorination of organic compounds, etc [1–3]. In addition, a combination of these two noble metals in one catalyst formulation appeared beneficial for a variety of catalyzed reactions, since bimetallic Pd-Pt systems demonstrated better catalytic performance than the respective monometallic catalysts in hydrodesulfurization [4–6], hydrogenation [7], alkane conversion [8] and oxidation of CO [9], $SO_2$ [10] and methane [11]. However, preparation and characterization of low metal loaded, highly dispersed supported bimetallic catalysts characterized by a considerable extent of alloying (for obtaining the best synergistic effects) still presents a difficulty [12]. For example, in spite of a single successful application [13], the use of diffraction methods for testing the degree of alloy homogeneity of Pd-Pt system is rather complicated because the lattice constants of both metals are very close to each other (0.389 nm vs. 0.392 nm, respectively).

In this work we addressed the problem of characterization of supported Pd-Pt alloy catalysts. To this end, silica was used as a model support. We decided to make use of chemical and catalytic probes which are much cheaper and accessible in many laboratories, and, what is more important, frequently more informative than physical probes in characterizing low metal loaded, highly dispersed supported metal catalysts.

## 2. Experimental

### 2.1. Catalysts preparation and pretreatment

The support was Davison 62 silica gel (60–75 mesh, 340 $m^2$/g surface area; 1.15 $cm^3$/g pore volume) washed with diluted HCl and redistilled water, dried in the oven at 290 K for 20 h, and finally, calcined in a fluidized bed in an air flow (400 $cm^3$/

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min) from RT to 723 K at a 3 K/min ramp and maintained at 723 K for 3 h.

The catalysts selected for investigation are listed in Table 1. The details of the preparation of these catalysts using incipient wetness (co)impregnation procedures or a direct redox method have been described previously [14] and [15], respectively. Catalysts prepared by impregnation had constant loading of $1.41*10^{-4}$ Mol of active component per 1 g of catalyst. Aqueous solutions (with volume corresponded with total pore volume of silica) of $PdCl_2$ (POCh Gliwice, Poland, analytical grade) and $H_2PtCl_6$ $6H_2O$ (Alfa Aesar; USA, high purity grade, 99.95%) were used for impregnation. During impregnation and preliminary drying with infrared lamps, a good mixing was assured by the rotary motion of a beaker containing the catalyst precursor. Then, the solid was further dried overnight in an oven at 363 K.

To obtain Pd-Pt/$SiO_2$ catalyst by direct redox method, DRM, the 1.5%Pd/$SiO_2$ catalyst (called "parent catalyst") was modified by addition of platinum in the reaction system similar to that described elsewhere [15]. Briefly, a palladium catalyst was prereduced in the reactor (50%$H_2$/Ar, 200 $cm^3$/min, 623 K, 1 h), purged in an Ar flow (200 $cm^3$/min, 663 K, 1 h), cooled in an Ar flow to room temperature and then immersed in redistilled water. The solution was continuously stirred by bubbling argon and an aqueous solution of $H_2PtCl_6$ was slowly introduced into the reactor. Then, concentrated $NH_4OH$ was added to adjust the pH 7 and the solution was stirred with bubbling argon for the next 20 min.

After preparation (by both methods, impregnation and direct redox method) and preliminary drying, the solids were precalcined in a fluidized bed in a 4%$O_2$/He stream (200 $cm^3$/min, 723K/3 h), purged in an Ar flow (200 $cm^3$/min, 673 K, 1 h) and prereduced in a 50%$H_2$/Ar stream (200 $cm^3$/min, 663K/1 h).

### *2.2. Catalysts characterization*

Prior to their characterization, the catalyst materials were reduced in wet hydrogen: the catalysts were wetted in a reactor with a few droplets of redistilled water and then reduced in a flow of mixture 50%$H_2$/Ar 100 $cm^3$/min (293 and 673 K at 8 K/min; 673 K/3 h). Preliminary experiments showed that by this pretreatment, it is possible to obtain metal particles similar in size in all catalysts. In addition, some metal sintering accompanied more extensive Pd-Pt alloying.

The catalysts were characterized by $H_2$ chemisorption, temperature programmed (palladium) hydride decomposition (TPHD) and tested in $CCl_2F_2$ hydrodechlorination. Finally, in X-ray diffraction (XRD) studies, the structure of post-reaction catalysts was compared with that of freshly reduced samples. Metal crystallite sizes from X-ray diffraction profile broadening were compared with metal particle sizes calculated from the chemisorption data ($d_{\mathrm{chem}} = 1.12/\mathrm{FE}$ [16,17]), see Table 1. Prior to reaction of dichlorodifluoromethane (CFC-12 from Galco S.A., Belgium; purity 99.9%) with hydrogen, all catalysts were reduced in flowing 10% $H_2$/Ar (25 $cm^3$/min), ramping the temperature from 20 to 673 K (at 8 K/min), and kept at 673 K for 1 h. The reaction was conducted in a glass flow system under atmospheric pressure. The flows of gases ($H_2$, Ar, $CCl_2F_2$) were fixed by MKS mass flow controllers to obtain feed partial pressures: 2 kPa for $CCl_2F_2$ and 20 kPa for $H_2$, in an argon carrier. The overall flow rate of the reactant gas mixture was 100 $cm^3$/min. In order to adequately establish changes in the catalytic behavior, a typical reaction run lasted ~20 h. The first stage of the reaction involved a 16 h period at 453 K. During this time the catalyst performance stabilized in a flow of the reaction mixture, as established by analyzing the reacting gas at 30 min intervals. The reaction mixture leaving the reactor was introduced onto a gas chromatograph (HP 5890 series II with FID) and analyzed using a 5% Fluorcol/Carbopack B column (10 ft) from Supelco. After 16 h of time-on-stream, the reaction temperature was lowered to 443 and 433 K and the next experimental points were collected. After catalyst screening at the lowest reaction temperature (433 K) the catalyst performance was tested again at 453 K, giving a good return to the initial behavior at this temperature. The mass of catalysts used for reaction was in range 0.1–0.4 g, depending on the catalyst activity, in order to maintain conversion levels in range 3–4.5% (at steady state). The relatively short screening time in combination with a low conversion was essential for silica support protection against significant corrosion. Apart from that the low conversion was indispensable to avoid secondary reactions.

## 3. Results and discussion

The following discussion on characterization of silica-supported Pd-Pt catalysts is based on the results obtained from three basic probes: the temperature-programmed (palladium) hydride decomposition (TPHD), changes in X-ray diffraction patterns of the Pd-Pt catalysts generated by catalytic reaction (hydrodechlorination of $CCl_2F_2$) and the catalytic behavior of differently prepared Pd-Pt catalysts. Two series of Pd-Pt/$SiO_2$ catalysts were compared, the impregnated ones with those prepared by a direct redox metod.

### *3.1. Temperature-programmed (palladium) hydride decomposition (TPHD)*

The concept of using TPHD studies to test alloy homogeneity of Pd-containing bimetallic catalysts is based on the common knowledge that adding another metal to palladium changes the propensity of the latter to form the β-hydride phase in hydrogen presence [18]. In general, even a small introduction of such metals like Ag, Au, Ni, Co to Pd reduces the amount of hydrogen in the β-hydride phase, expressed as H/Pd. In addition, the conditions of formation and decomposition of β-hydride phases ($H_2$ pressure at a given temperature) change upon Pd doping. It was found that, e.g. the β-PdAuH is more stable than the β-PdH [19], whereas after adding Pt to Pd, the situation is reverse [20]. The work by Noh et al. [20] indicates that alloying Pd with Pt leads to an increase of the plateau pressures, characteristic of the β-hydride phase formation. More specifically, at the temperature 303 K (which

Table 1
$Pd\text{-}Pt/SiO_2$ catalysts, their composition and physicochemical characterization

| Catalyst[a] | Chemisorption[c] | | TPHD[d] | | XRD analysis of metal phases | | Conclusions from TPHD and XRD studies |
|---|---|---|---|---|---|---|---|
| | FE | $d_{chem}$, nm | H/Pd | $T_{min}$, K | After reduction | After reaction | |
| 1.50 wt% $Pd/SiO_2$(IMP)[b] | 0.11 | 10.5 | 0.48 | 347 | Pd crystallites of ~10 nm | $PdC_x$ phase at 239.3° ($2\theta$) | Good agreement between $d_{chem}$ and $d_{XRD}$, and a relatively narrow TPHD peak ⇒ very homogeneous in size Pd particles |
| 1.63 wt% $Pd_{90}Pt_{10}/SiO_2$(IMP)[b] | 0.06 | 18.4 | 0.42 | 338 | A slightly asymmetric (1 1 1) reflection from Pd-Pt phase with maximum at 40.1° ($2\theta$) | A peak from Pt (or Pt-rich phase) at ~40° and a diffuse reflection peak from a $PdC_x$ phase at 39.3° | H/Pd from TPHD characteristic for pure Pd. After reaction only Pd was transformed into $PdC_x$, platinum left unchanged. ⇒ Very little (if any) PdPt alloying. |
| 1.75 wt% $Pd_{80}Pt_{20}/SiO_2$(IMP)[b] | 0.06 | 18.1 | 0.29 | 335 | as above | An intensive reflection peak from Pt-rich phase (39.9°) + diffuse peak from a $PdC_x$ phase at 39.2° | Similar situation as above, although some small amount of Pt alloyed with Pd |
| 1.87 wt% $Pd_{70}Pt_{30}/SiO_2$(IMP)[b] | 0.06 | 18.7 | 0 (0[e]) | No $H_2$ release | An asymmetric (1 1 1) peak of Pd-Pt phase ⇒ coexistence of different $Pd_xPt_{1-x}$ phases | XRD profile nearly unchanged after hydrodechlorination | No hydride decomposition ⇒ sintering of the catalyst in wet $H_2$ leads to a positive (but not complete ⇐ XRD) PdPt alloying. |
| 2.01 wt% $Pd_{60}Pt_{40}/SiO_2$(IMP)[b] | 0.05 | 21.2 | 0 (0[e]) | As above | As above | As above | As above |
| 2.75 wt% $Pt/SiO_2$(IMP)[b] | 0.04 | 32.6 | 0 | As above | Pt crystallites of ~25 nm | Pt crystallites of ~25 nm | Fair agreement between $d_{chem}$ and $d_{XRD}$ ⇒ an apparent absence of very small Pt particles |
| 1.65 wt% $Pd_{95}Pt_5/SiO_2$(DR)[b] | 0.08 | 13.7 | 0.13[e] | 290 | A symmetric (1 1 1) peak of Pd-Pt phase (crystallite size $d_{XRD}$ ~11 nm) with maximum at 40° | An asymmetric peak with maximum at 39.2° | Fair agreement between $d_{chem}$ and $d_{XRD}$ and evolution of $H_2$ during TPHD at very low temperature ⇒ a considerable PdPt alloying |
| 2.17 wt% $Pd_{80}Pt_{20}/SiO_2$(DR)[b] | 0.08 | 13.5 | 0[e] | No $H_2$ release | A symmetric (1 1 1) peak of Pd-Pt phase (crystallites of ~16 nm) with maximum at 40° | A rather symmetric (1 1 1) peak with maximum at 39.3° | Good agreement between $d_{chem}$ and $d_{XRD}$ and no evolution of $H_2$ during TPHD ⇒ a nearly complete PdPt alloying |

[a] In catalyst designation, the first number indicates the total metal wt.% and subscripts (for PdPt catalysts) denote atom percentages of Pd and Pt in metal phase.

[b] Acronyms IMP and DR denote preparation method of the catalyst, e.g. incipient wetness impregnation and direct redox method, respectively (see text).

[c] In subcolumns FE = metal fraction exposed [$H_{ads}/(Pd + Pt)$], $d_{chem}$ (metal particie size) calculated as 1.12/FE [16,17].

[d] In subcolumns, H/Pd shows the ratio of moles of $H_2$ released during TPHD trace to moles of Pd, $T_{min}$—shows the position of minimum in the trace.

[e] Selected TPHD runs with starting temperature ~273 K (typical experiments started at room temperature).

is close to room temperature, a convenient starting temperature in temperature programmed studies) the alloy with only 5 at.% Pt should not form the β-hydride phase at the hydrogen pressure below 12 kPa (Fig. 7 in Ref. [20]). Because the $H_2$/Ar mixture used in our TPHD studies contained ca. 10 kPa of hydrogen, it appears that preparation of perfectly mixed Pd-Pt catalysts should lead to featureless TPHD profiles, i.e. without any peaks demonstrating hydrogen release during hydride decomposition. However, this was not the case for the Pd-Pt/$SiO_2$ catalysts prepared by incipient wetness impregnation (Fig. 1). Large amounts of released hydrogen from $Pd_{90}Pt_{10}$(IMP) and $Pd_{80}Pt_{20}$(IMP) clearly indicate a poor Pd-Pt mixing in these catalysts. Though the $Pd_{70}Pt_{30}$(IMP) and $Pt_{60}Pt_{40}$(IMP) exhibit featureless TPHD profiles it is still difficult to conclude about good alloying in these catalysts, because, as was mentioned, only 5 at.% of dissolved platinum should annihilate the hydride formation. On the other hand, the Pd-Pt catalysts prepared by the direct redox method appeared much better alloyed, as the TPHD traces from these catalysts appeared very flat (Fig. 1, see TPHD runs started at room temperature).

The results of Noh et al. [20] indicate that at $H_2$ pressure used in our studies, the $Pd_{95}Pt_5$ alloy should be transformed to the respective hydride at 273 K. Therefore, additional TPHD experiments with using 273 K as a starting temperature should detect the presence of Pd-Pt phases with Pt content of ~5 at.% in all samples which exhibited featureless TPHD traces when experiments were started at room temperature. The results are included in Fig. 1 (and Table 1). It appears that the $Pd_{95}Pt_5$(DR) shows a shallow minimum at ~290 K, indicating the effect of Pt incorporation to Pd. On the other hand, a featureless TPHD trace of the $Pd_{80}Pt_{20}$(DR) speaks against the presence of ≤5 at.% Pt phase(s), however a more Pt-rich phases (like 10 at.% Pt) may be present there. In any case, TPHD clearly demonstrates that the $Pd_{80}Pt_{20}$(DR) is much better alloyed than the $Pd_{80}Pt_{20}$(IMP), evidencing a superiority of alloy preparation by the direct redox method. Similar TPHD experiments with $Pd_{70}Pt_{30}$(IMP) and $Pd_{60}Pt_{40}$(IMP) did not show any hydride formation at 273–293 K, excluding the presence of ≤5 at.% Pt phase(s) (Fig. 1).

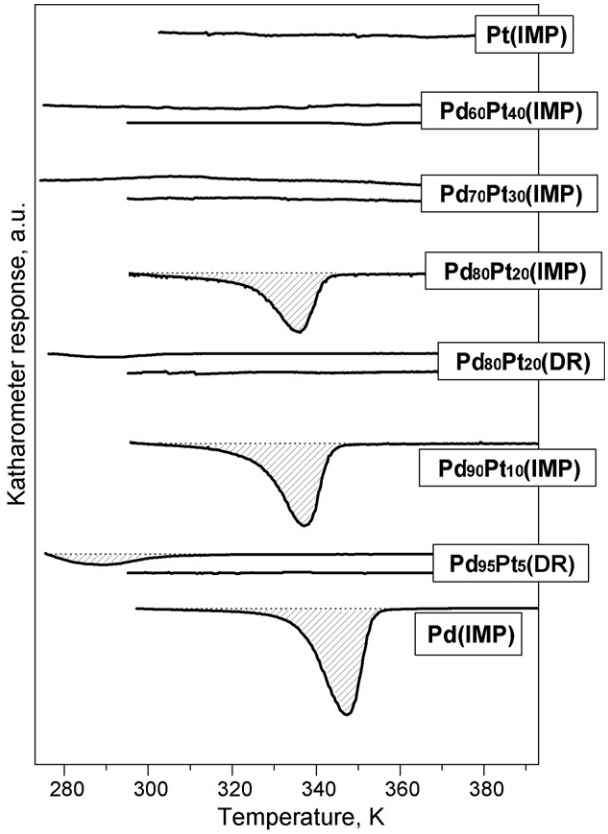

Fig. 1. TPHD profiles of Pd-Pt/$SiO_2$ catalysts. In selected cases the starting TPHD temperature was lowered from room temperature to 273 K.

### 3.2. Catalytic hydrodechlorination (HdCl) of dichlorodifluoromethane (CFC-12)

The results of catalytic screening of all tested catalysts are shown in Fig. 2. Steady state catalytic activities, after overnight

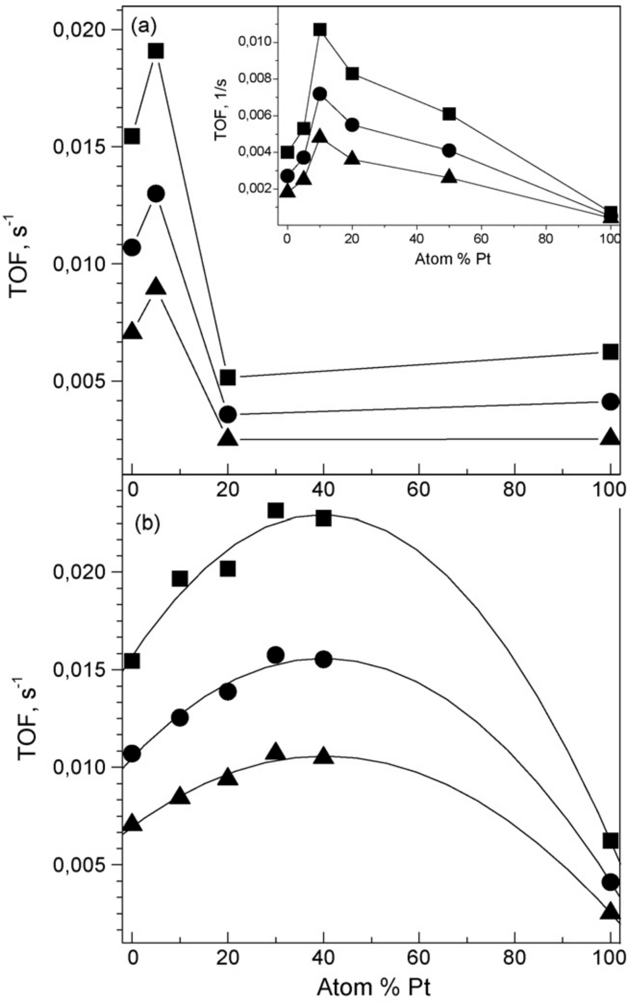

Fig. 2. The effect of Pd-Pt alloy composition on the activity of Pd-Pt/$SiO_2$ catalysts in hydrodechlorination of $CCl_2F_2$. (a) Pd-Pt catalysts prepared by the direct redox method (inset: the relation for Pd-Pt/$Al_2O_3$ catalysts from Ref. [21]), (b) Pd-Pt catalysts prepared by impregnation. Reaction temperatures: 453 K (squares), 443 K (circles) and 433 K (triangles).

screening, are presented as turnover frequencies. Variations in product selectivities were rather small (e.g. selectivity to $CH_2F_2$ was 40 ± 10% for all catalysts at 453 K) and are not discussed. Fig. 2a shows TOF data for the Pd-Pt/$SiO_2$ catalysts prepared by the direct redox method, whereas Fig. 2b collects the respective data for samples prepared by impregnation. Maxima in the TOF-alloy composition relations (present in all reaction temperatures) reveal the presence of synergistic effect, i.e. imply a positive Pd-Pt alloying, no matter which preparation method was used. A more abrupt decrease of TOF on alloying seen in Fig. 2a in combination with better alloy homogeneity of DR samples suggest that the maximum of TOF would occur for homogeneous Pd-Pt alloys at near 10 at.% Pt. Inset in Fig. 2b reminds our earlier data obtained for Pd-Pt/$Al_2O_3$ catalysts [21].

### *3.3. X-ray diffraction of reduced and used Pd-Pt/$SiO_2$*

As mentioned in Section 1, very similar lattice parameters of Pd and Pt make the XRD technique rather less useful for probing the extent of Pd-Pt alloying. A single successful XRD study of this alloy system [13] make use of (3 3 1) reflections of both metals which are reasonably well separated and located around $2\theta \approx 118^\circ$ (for Cu Kα radiation). In our case, these XRD reflections were so small that it was impossible to make use of them. Based on (1 1 1) and (2 0 0) reflections we tried to characterize metal phases in our catalysts after reduction (phase composition and metal crystallite size) and the respective results are in Table 1. More importantly, we were rather interested in shifts in XRD reflections caused by metal carbiding during hydrodechlorination. It is known, that in course of $CCl_2F_2$ hydrodechlorination over Pd-containing catalysts, palladium is transformed into fcc $PdC_x$ solution, where $x$ may reach 0.13 [19,22]. The most important results are shown in Fig. 3. It is clearly shown than the $Pd_{80}Pt_{20}$(DR) is much better alloyed than $Pd_{80}Pt_{20}$(IMP). For the latter hydrodechlorination drives a part of Pd-richer material to a respective Pd(rich)-$C_x$ solution (shift towards lower diffraction angles), but a Pt-rich reflection stays unchanged (Pt does not dissolve carbon at these conditions). It clearly speaks for poor alloy homogeneity in the case of $Pd_{80}Pt_{20}$(IMP). Upper XRD spectra (in Fig. 3) show the behavior of $Pd_{95}Pt_5$(DR) catalyst. Shapes of reflections, as well as the fact that the entire diffraction peak is shifted towards lower angles, demonstrate that alloy homogeneity is good.

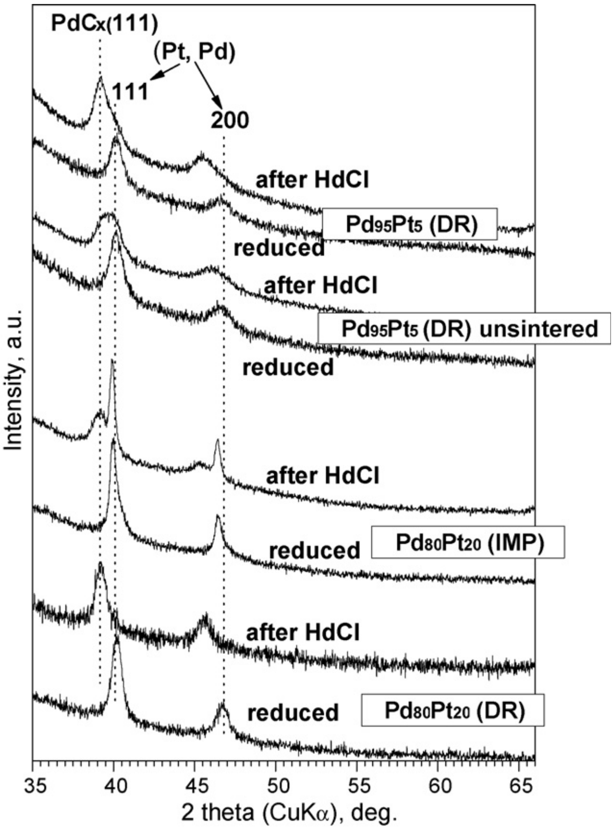

Fig. 3. XRD patterns for selected Pd-Pt/$SiO_2$ catalysts. Spectra of reduced catalysts were compared with those of post-reaction sample (after HdCl).

## 4. Conclusions

1. TPHD method showed for diagnosing the extent of alloying in Pd-Pt/$SiO_2$ catalysts. Introduction of Pt to Pd catalysts moves the TPHD peak gradually towards lower temperatures and the shift in hydride decomposition peak is accompanied by a decrease in the amount of released hydrogen.
2. XRD of post-reaction Pd-Pt/$SiO_2$ catalysts showed transformation of Pd-rich phases into respective Pd-$C_x$ solutions.
3. The observed correspondence of TPHD and X-ray diffraction data for silica-supported Pd–Pt catalysts makes the both techniques feasible and supplementary for diagnosing the quality of Pd–Pt alloying.
4. The synergistic effect observed in the hydrodechlorination of $CCl_2F_2$ proves the formation of mixed Pd-Pt ensembles.

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## References

[1] S. Nishimura, Handbook of Heterogeneous Catalytic Hydrogenation for Organic Synthesis, Wiley, New York, 2001, pp. 29.
[2] V. Ponec, G.C. Bond, Catalysis by metals and alloys, Studies in Surface Science and Catalysis, vol. 95, Elsevier, Amsterdam, 1995, pp. 604.
[3] V.I. Kovalchuk, J.L. d'Itri, Appl. Catal. A 271 (2004) 13.
[4] T. Kabe, W. Qian, Y. Hirai, L. Li, A. Ishihara, J. Catal. 190 (2000) 191.
[5] A. Ishihara, F. Dumeignil, J. Lee, K. Mitsuhashi, E.W. Qian, T. Kabe, Appl. Catal. A 289 (2005) 163.
[6] A. Niquille-Röthlisberger, R. Prins, J. Catal. 242 (2006) 2007.
[7] B. Pawelec, R. Mariscal, R.M. Navarro, S. Van Bokhorst, S. Rojas, J.L.G. Fierro, Appl. Catal. A 225 (2002) 223.
[8] T. Kościelski, Z. Karpiński, Z. Paál, J. Catal. 77 (1982) 539.
[9] M. Yashima, L.K.L. Falk, A.E.C. Palmqvist, K. Holmberg, J. Colloid Interf. Sci. 268 (2003) 348.

[10] S. Koutsopoulos, K.M. Eriksen, R. Fehrman, J. Catal. 238 (2006) 270.

[11] G. Lapisardi, L. Urfels, P. Gelin, M. Primet, A. Kaddouri, E. Garbowski, S. Toppi, E. Tena, Catal. Today 117 (2006) 564.

[12] V. Ponec, G.C. Bond, Catalysis by metals and alloys, Studies in Surface Science and Catalysis, vol. 95, Elsevier, Amsterdam, 1995, pp. 339.

[13] A.E. Cordero-Borboa, E. Sterling-Black, A. Gómez-Cortés, A. Vázquez-Zavala, Appl. Surf. Sci. 220 (2003) 174.

[14] M. Bonarowska, J. Pielaszek, W. Juszczyk, Z. Karpiński, J. Catal. 195 (2000) 304.

[15] C. Micheaud, M. Guerin, P. Marecot, C. Geron, J. Barbier, J. Chim. Phys. 93 (1996) 1394.

[16] S. Ichikawa, H. Poppa, M. Boudart, J. Catal. 91 (1985) 1.

[17] W. Rachmady, M.A. Vannice, J. Catal. 192 (2000) 322.

[18] F. Lewis, Palladium-Hydrogen System, Academic Press, New York, 1967.

[19] M. Bonarowska, J. Pielaszek, V.A. Semikolenov, Z. Karpiński, J. Catal. 209 (2002) 528.

[20] H. Noh, T.B. Flanagan, T. Sonoda, Y. Sakamoto, J. Alloys Comp. 228 (1995) 164.

[21] M. Legawiec-Jarzyna, A. Śrębowata, W. Juszczyk, Z. Karpiński, Catal. Today 88 (2004) 93.

[22] E.J.A.X. van de Sandt, A. Wiersma, M. Makkee, H. Van Bekkum, J.A. Moulijn, Catal. Today 35 (1997) 163.