

Hydrodechlorination of Tetrachloromethane Over Supported Platinum Catalysts. Effects of Hydrogen Partial Pressure and Catalyst's Screening Protocol on the Catalytic Performance

Magdalena Bonarowska · Zbigniew Karpinski

Published online: 27 July 2012

© The Author(s) 2012. This article is published with open access at Springerlink.com

Abstract Two series of silica- and alumina-supported platinum catalysts were investigated in the hydrodechlorination (HdCl) of tetrachloromethane. During an initial period of reaction carried out at a lower H_2/CCl_4 ratio the catalysts, especially those characterized by high metal dispersion, deactivated with time-on-stream. Two catalyst screening protocols were used. The first one concerned a gradually increased hydrogen partial pressure, whereas during the second one the H_2 pressure was decreased. Although, in general, the hydrogen-rich reaction conditions resulted in improved catalyst performance (higher overall activity and selectivity to $CHCl_3$), the second protocol led to even better results. Reasons for such a behaviour are suggested. Because of very high activity of a few tested samples, changes in CCl_4 conversion with the hydrogen partial pressure do not reflect real reaction orders in hydrogen. The same reason may lead to falsification of apparent activation energies. In certain cases the relation between conversion and hydrogen pressure showed a maximum, suggesting that HdCl undergoes via a Langmuir–Hinshelwood mechanism, when hydrogen and CCl_4 compete for metal surface sites. Both carbon- and chlorine-containing deposits were found in the post-reaction catalyst samples.

Keywords CCl_4 · Hydrodechlorination · Platinum catalysts · Alumina · Silica · Effect of metal dispersion · Effect of hydrogen pressure, activation energy

1 Introduction

Recently we have shown that catalytic activity of Pt/Al_2O_3 in CCl_4 hydrodechlorination (HdCl) exhibits very strong inverse relationship with metal dispersion; highly dispersed Pt samples exhibit very low turnover frequencies [1]. A similar, but a much milder trend, was found for silica-supported Pt catalysts. This significant support effect was attributed to an extensive surface chloriding of small Pt particles interacting with Lewis acid sites of γ -alumina. It was proposed that such interactions lead to the formation of electrodeficient Pt sites, which are quickly blocked by produced chloride species. On silica, similar in kind metal-support interactions do not occur, and, in effect, deactivation of Pt/SiO_2 catalysts is less marked. These results were in line with previously published data by Zhang and Beard [2] for Pt/Al_2O_3 catalysts with varied metal dispersions and by Prati and Rossi [3] who showed an exceptional catalytic behavior of Pt/Vycor glass (96 % silica).

The idea that catalyst deactivation is caused by chloride species seems to be supported by the results obtained for CCl_4 HdCl on $Pt-Au/Al_2O_3$ catalysts [4]. A higher activation energy for monometallic Pt/Al_2O_3 (56 vs. ~ 30 kJ/mol for the bimetallics) suggests that chlorine removal from Pt surface would be more difficult for Pt only surface than for bimetallic Pt–Au surface, in line with the magnitude of metal-chlorine bond energy ($E_{Pt-Cl} > E_{Au-Cl}$). However, the ultimate evidence as to the reason of catalyst deactivation

M. Bonarowska (✉) · Z. Karpinski
Institute of Physical Chemistry of the Polish Academy of Sciences, ul. Kasprzaka 44/52, 01224 Warsaw, Poland
e-mail: mbonarowska@ichf.edu.pl

Z. Karpinski
e-mail: zkarpinski@ichf.edu.pl

Z. Karpinski
Faculty of Mathematics and Natural Sciences, School of Science, Cardinal Stefan Wyszyński University, ul. Wóycickiego 1/3, 01938 Warsaw, Poland

(chloride or carbonaceous species) was not provided so far, so it is still a matter of opinion.

In this respect a considerable part of published data seem to be in an apparent conflict with the aforementioned results [1–3]. Very good HdCl performance of highly dispersed Pt/Al₂O₃ catalysts was reported by various groups [5–7]. Choi et al. [5] showed that the kind of metal precursor is more important factor in shaping the HdCl behavior than the size of metal particles. Pt particles of very small size (~1 nm) supported on alumina, prepared from Pt(II) precursors, showed stable, high conversion of CCl₄ above 99 % and selectivity to CHCl₃ above 78 % and a retarded coke formation, compared to that from H₂PtCl₆. Analogous results have recently been reported by Bae et al. [8].

Among various factors influencing the HdCl behavior of supported platinum catalysts one should also consider the reaction conditions, such as contact time, reaction temperature, the H₂/CCl₄ ratio in the reaction mixture and the protocol of catalyst's screening. Shorter contact times allow to keep low conversion levels and to extract useful information about the reaction mechanism from the selectivity pattern, without considering secondary reactions, such as CH₂Cl₂ formation in HdCl of CCl₄ on Pt/Al₂O₃ found by Dal Santo et al. [7]. Higher reaction temperatures, i.e. >393 K in the case of CCl₄ HdCl, lead to a complete conversion and to more extensive catalyst deactivation. This detrimental effect is softened by working with hydrogen-rich reaction mixtures (e.g. H₂/CCl₄ ratio = 9, [5]).

It must be stressed that the HdCl of CCl₄ was investigated by us [1, 4] at a relatively low reaction temperature, 343–363 K. Our intention was to avoid operation at very high reactant conversions, i.e. at nearly 100 %, easily reachable for HdCl of CCl₄ at the reaction temperatures ≥400 K (e.g. [7–9]). However, even at such relatively mild reaction conditions (≤363 K and the feed H₂/CCl₄ ratio ~7) a considerable catalyst deactivation was observed. It must be recalled that the H₂/CCl₄ molar ratio ~7 was intentionally used by us because a similar reactant ratio was used in the studies we wished to refer to [2, 3]. However, it is well known that the H₂/CCl₄ molar ratios higher than 7 reduce catalyst deactivation [5–7]. The aim of this work was the reinvestigation of the same series of alumina- and silica-supported platinum catalysts (as in [1]) in the HdCl of CCl₄, at different reaction temperatures and H₂/CCl₄ molar ratios. Less surface deactivation expected at hydrogen-rich conditions should be manifested by higher overall activity and CHCl₃ selectivity (at the expense of dimeric species formation). During the realization of this program we found that the catalyst's screening protocol may also have a considerable effect on the catalytic behavior of Pt catalysts.

2 Experimental

2.1 Preparation and Characterization of the Catalysts

Preparation and characterization (by CO chemisorption, XRD and TEM) of two series of 1.5 wt% metal-loaded Pt catalysts was reported in [1]. Briefly, they were prepared by incipient wetness of alumina (Sasol Puralox SCCA, 150–200 mesh, 196 m²/g) and silica (Davison 62, 120–200 mesh, 268 m²/g) with an aqueous solution of H₂PtCl₆. After impregnation, Pt/SiO₂ and Pt/Al₂O₃ precursors were divided into small parts, and by combination of different conditions of calcination, reduction and sintering (in Ar or wet H₂) two series of catalysts with platinum dispersion in a relatively wide range were obtained [1]. In this study only selected samples from two series of 1.5 wt% metal-loaded Pt catalysts were subjected to catalyst screening. Table 1 shows the basic characteristics of selected samples, keeping the same catalyst designation as in the previous work [1]. CO chemisorption was used for assessing metal dispersions and Pt particle sizes. For the silica-supported series, Pt particle size was mostly confirmed by XRD diffraction studies. Transmission electron microscopy provided essential information about metal particle growth in platinum catalysts subjected to various regeneration pretreatments [1]. In addition, the previous work showed that a prolonged screening of supported Pt catalysts in HdCl of CCl₄, at a relatively low reaction temperature (343–363 K), does not lead to detectable metal sintering. Kinetic results obtained in the present study will be discussed in the light of catalyst characterization obtained in that previous work [1].

After kinetic runs the catalysts were investigated by a temperature-programmed hydrogenation (TPH), followed by mass spectrometry (MA200, Dycor-Ametek, Pittsburgh, USA), to detect species which could be removed by hydrogen from the catalysts used. TPH runs were performed by flowing a 20 % H₂/He mixture (25 cm³/min) at a 10 °C/min ramp. In TPH runs of the used catalysts (samples ~0.085 g), attention was paid to *m/z* 15 and 16 (methane evolution), and *m/z* 36 and 38, which are suggestive of HCl liberation from the catalysts used.

2.2 Catalytic Tests

Prior to the reaction, the catalyst sample was dried at 393 K for 0.5 h in an argon flow and reduced in flowing 20 % H₂/Ar (25 cm³/min), ramping the temperature from 393 to 673 K (at 8 K/min) and kept at 673 K for 2 h. The reaction of HdCl of tetrachloromethane (analytical reagent from POCh, Gliwice, Poland, purity, >99.6 %), provided from a saturator maintained at 273 K and bubbled in a flow of H₂ + Ar mixture (29 cm³/min, with variable H₂-to-Ar

Table 1 Characteristics of 1.5 wt% Pt/Al₂O₃ and 1.5 wt% Pt/SiO₂ catalysts [1]

Catalyst designation	Catalyst pretreatment: drying/calcination, prereduction, sintering (if employed)	CO chemisorption	
		FE ^a	d_{Pt}^b (nm)
A1	O ₂ , RT/673 K (5 K/min); 673 K, 0.5 h; 10 % H ₂ /Ar, RT/623 K (1 K/min); 623 K, 2 h	0.691	1.6
A6	As A1 + Ar, RT/773 K (8 K/min); 773 K, 0.5 h	0.361	3.1
A9	No calcination; H ₂ , RT/673 K (5 K/min); 673 K, 2 h	0.13	8.7
S1	O ₂ , RT/673 K (8 K/min); 673 K, 0.5 h; 10 % H ₂ /Ar, RT/623 K (2 K/min); 623 K, 2 h	0.893	1.3 ^c
S8	As S1 + Ar, RT/803 K (8 K/min); 803 K, 7 h	0.264	4.3 (4.3 ^d)
S11	No calcination; wet H ₂ , RT/673 K (20 K/min); 673 K, 2 h	0.143	7.9 (7.4 ^d)

Details of catalyst pretreatment and metal dispersion from CO chemisorption and XRD investigation

^a (Platinum) FE from CO chemisorption (FE = CO_{ad}/Pt_t)

^b Pt particle size $d_{Pt} = 1.13/FE$ (Rachmady et al. [23])

^c Invisible XRD reflections from platinum

^d Pt crystallite sizes from the 111 reflection broadenings using the Scherrer formula (nearly identical before and after reaction)

ratios, permitting a hydrogen partial pressure study) was carried out at atmospheric pressure, in a glass flow reactor. The reaction (at 363 K and below) was followed by gas chromatography (HP 5890 series II with FID, a 5 % Fluorcol/Carbopack B column (10 ft) from Supelco). The flows of H₂ and Ar (all 99.999 % pure, further purified by passing through MnO/SiO₂ traps), were maintained by mass flow controllers (MKS). Two catalyst's screening protocols were used. The first procedure was a catalyst testing using H₂/CCl₄ partial pressure ratio of 6.7 (30.1/4.47 kPa), i.e. as in our previous studies [1, 4]. After catalyst screening at 363 K overnight and reaching a steady state, the temperature was gradually decreased to 353 and 343 K, and new experimental points were collected. Then, the H₂/CCl₄ ratio was increased to ~13.4 (60.1/4.47 kPa), and next experimental points were collected. In the second protocol the catalysts were first investigated starting from the highest H₂/CCl₄ ratio, ~21.7 (96.9/4.47 kPa), and then

the catalyst screening was followed at a steadily decreasing H₂/CCl₄ ratio: 13.4, 6.7 and ~4.5 (~20/4.47 kPa). Rather short contact time (V/F), ~0.26 s was applied. Duration of a single catalyst screening run was between ~90 and ~200 h.

In a specially designed experiment, one Pt/Al₂O₃ catalyst characterized by small metal particles (<2 nm, A1) was investigated after pretreating it with HCl + H₂ mixture at the temperature 363 K for 2 h. To this aim, HCl was produced in situ from CCl₄ and H₂, in an upstream located reactor, filled with another portion of Pt/Al₂O₃, which operated at 573 K. This procedure, taken from [9], generates HCl and methane, according to the reaction: CCl₄ + 4H₂ → 4HCl + CH₄. Large amounts of produced methane should not block platinum sites at such low temperature as 363 K and at high hydrogen pressure. Previous works on methane/deuterium exchange on platinum [10, 11] showed that the reaction goes via a stepwise

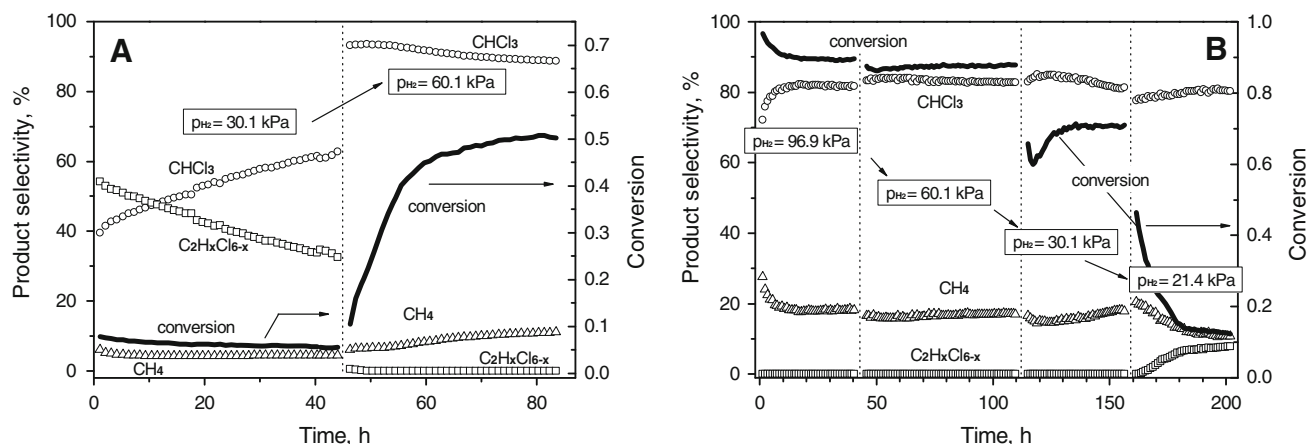


Fig. 1 Time on stream behavior of the 1.5 % Pt/Al₂O₃ catalyst (A1, FE = 0.691) in CCl₄ HdCl at 363 K. For catalyst notation see Table 1. **a** Catalyst screening at the H₂/CCl₄ ratios 6.7:1 ($P_{H_2} = 30.1$ kPa) and

13.4:1 ($P_{H_2} = 60.1$ kPa)—upward trend. **b** The gradual downward change in P_{H_2} , from $P_{H_2} = 96.9$ kPa (H₂/CCl₄ ratio = 21.7) to $P_{H_2} = 21.4$ kPa (H₂/CCl₄ ratio = 4.8)

mechanism, i.e. it involves the participation of reversibly adsorbed methyl radicals, which should be easily removed from the catalyst surface by flushing it with hydrogen.

3 Results and Discussion

Table 1 shows the basic characteristics of six supported platinum catalysts selected from a larger representation of platinum catalysts used in [1]. A large variety of conditions of sample pretreatment resulted in preparation of catalysts, characterized by an extensive range of metal dispersion. The catalysts chosen for the present study cover the most interesting (from the catalytic standpoint) range of metal particle sizes, from <2 to ~ 8 nm, therefore their catalytic behavior should also reflect expected surface-sensitivity effects.

Our previous studies [1] on HdCl of CCl_4 on supported Pt catalysts were performed using a standard H_2/CCl_4 ratio $\sim 7:1$. In the present study the same catalysts were investigated at different hydrogen partial pressures. Figure 1 (left section) shows that at the beginning this Pt/ Al_2O_3 catalyst (characterized by very small Pt particles, <2 nm) exhibits strong deactivation with time-on-stream. In addition, the selectivity towards dimeric $\text{C}_2\text{H}_x\text{Cl}_{6-x}$ products (mainly C_2Cl_6 and $\text{C}_2\text{H}_2\text{Cl}_4$) is high, although somewhat decreasing during the long-term testing. The selectivity for chloroform (desired product) is rather modest, not exceeding 60 %. The overall conversion level at a quasi-steady state is only ~ 0.05 . Such a catalytic behavior was attributed to an extensive surface chloriding of small Pt particles interacting with Lewis acid sites of γ -alumina [1]. It was also suggested that such interactions lead to the formation of electrodefficient Pt sites, which are quickly blocked by the produced chloride species.

The increase of hydrogen pressure by factor of 2 radically changes the catalytic performance of this highly dispersed alumina-supported catalyst, as it is seen in Fig. 1a. The overall conversion levels, established during the lower H_2/CCl_4 ratio (6.7; 30.1/4.47 kPa) screening, start to increase gradually and after ~ 20 h of reaction attain a rather high value, ~ 0.5 . At the same time, the selectivity towards chloroform reaches ~ 90 % and C_2 -dimers nearly cease from the reaction products. An order of magnitude increase of the overall reaction rate cannot be rationalized when one assumes a slightly positive (fractional) reaction order in hydrogen found in the kinetic studies of HdCl reactions [12, 13]. A rough calculation of present data (only two experimental points!) would suggest that the reaction order in H_2 is higher than 3, which does not seem a trustworthy value. In addition, a gradual and rather long-lasting improvement clearly indicates that

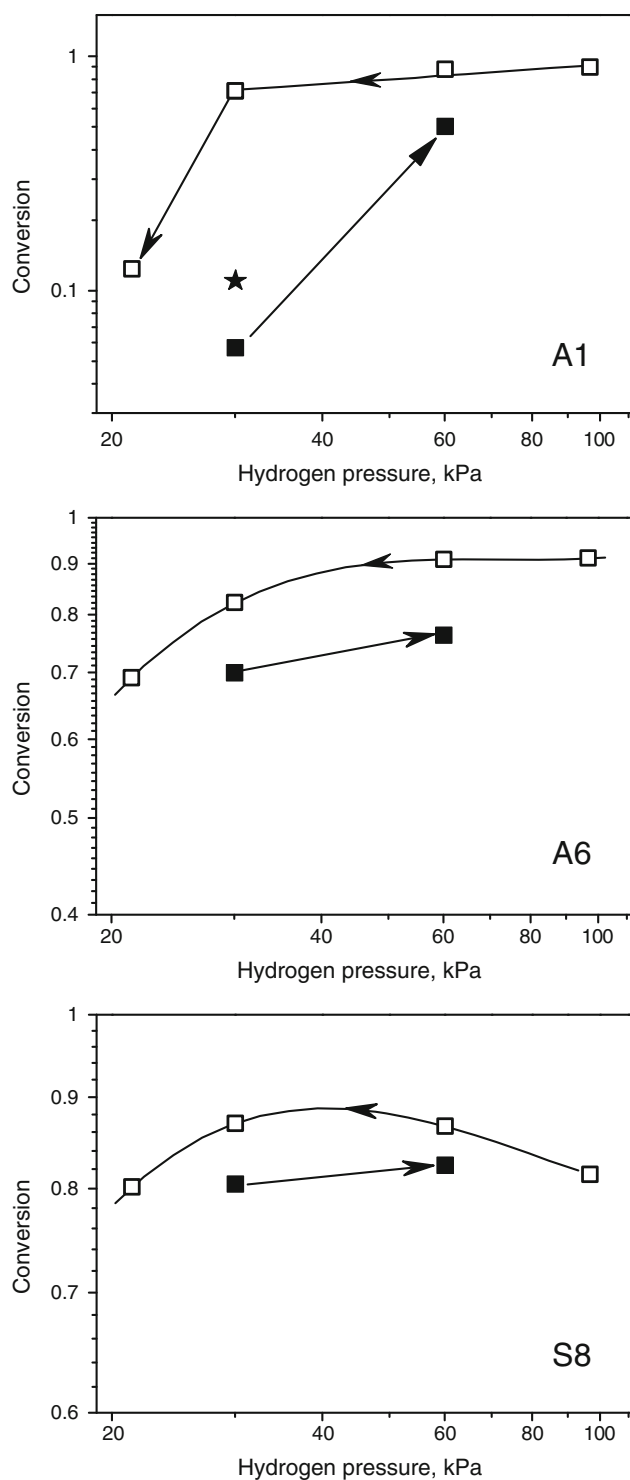


Fig. 2 Changes in catalytic activity in HdCl of CCl_4 for three selected platinum catalysts (A1, A6 and S8) associated with different catalyst screening protocol (downward or upward variations in P_{H_2}). Reaction temperature 363 K. For catalyst notation see Table 1. *Single star* shown in upper section shows the catalytic behavior of catalyst A1 subjected to HCl pretreatment

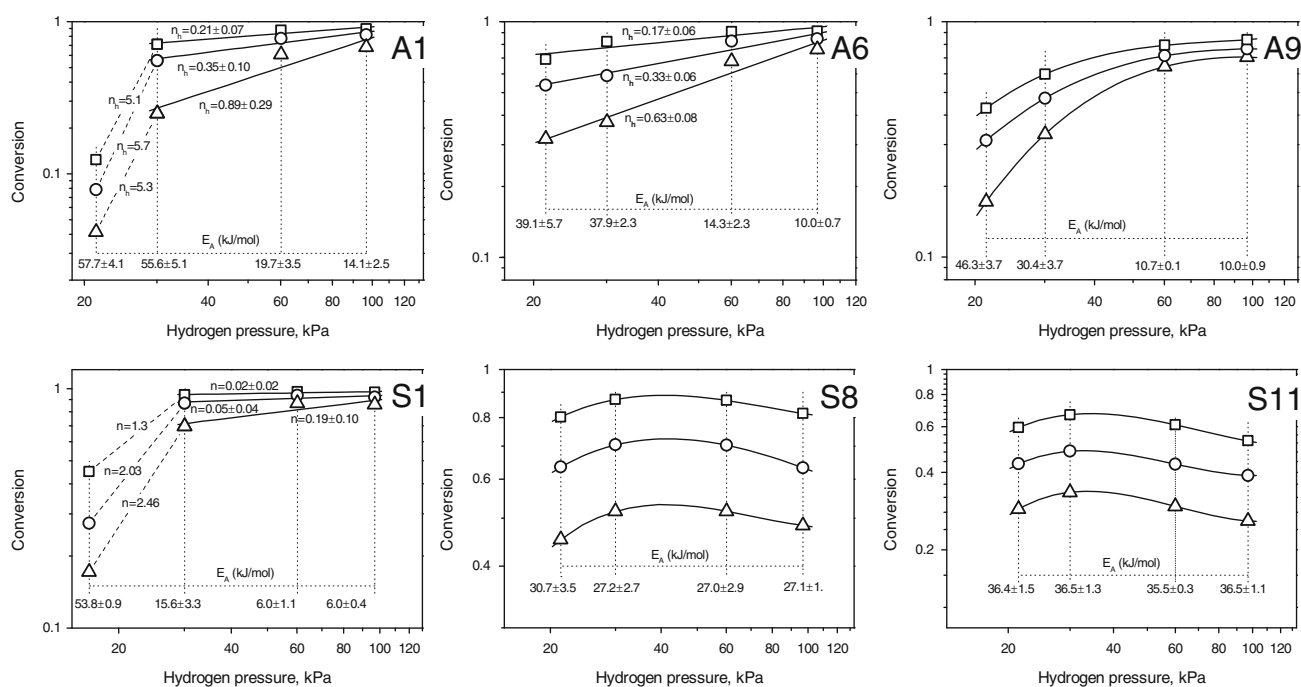


Fig. 3 Hydrogen pressure effect on conversion level in HdCl of CCl_4 at different reaction temperatures (363, 353 and 343 K: squares, circles and triangles, respectively) for alumina (A1, A6, A9) and

silica (S1, S8, S11) supported platinum catalysts. For catalyst notation see Table 1. Apparent activation energies (E_A 's) refer to all hydrogen partial pressure conditions

significant changes take place on the catalyst's surface, considered as a slow removal of unreactive surface species.

On the other hand, if catalyst screening is realized with downward variation of hydrogen pressure, starting from $P_{\text{H}_2} = 96.9$ kPa (at H_2/CCl_4 ratio = 21.7), overall changes in the catalytic behavior are different from the previous situation (Fig. 1b). A very high conversion level (~ 0.9) observed for $P_{\text{H}_2} = 96.9$ and 60.1 kPa decreases only to ~ 0.7 after the respective hydrogen pressure change to 30.1 kPa (at H_2/CCl_4 ratio = 6.7). Compared with the upward variation of hydrogen pressure (conversion ~ 0.05 at P_{H_2} 30.1 kPa), this high conversion level is accompanied by a large improvement in CHCl_3 selectivity and an apparent absence of C_2 -dimeric species. Only when the hydrogen pressure was decreased to 21.4 kPa (at H_2/CCl_4 ratio = 4.8), the level of conversion drops to ~ 0.12 , with simultaneous appearance of C_2 -dimeric products. Similar situations were observed for a highly dispersed Pt/ SiO_2 catalyst (S1) and the other two Pt/ Al_2O_3 catalysts (A6 and A9), however respective changes in the catalytic behavior were not as large as for the catalyst A1. 1.5 wt% Pt/ SiO_2 catalyst characterized by the highest metal dispersion (S1) strongly deactivates during first minutes of reaction (the decrease in conversion from ~ 0.9 to 0.2, results not graphically presented). However, after ~ 1 h of time-on-stream its catalytic performance gradually undergoes a significant improvement, reaching ~ 0.8 conversion and a similar level of CHCl_3 selectivity. Such a behavior would

be explained by a fast initial deactivation of small Pt particles (as also seen for the highly dispersed Pt/ Al_2O_3 catalysts) caused by an immediate deposition of unreactive species. However, the further progress of reaction, still with H_2/CCl_4 ratio of 6.7 ($P_{\text{H}_2} = 30.1$ kPa), allows the restoration of a very high activity of this catalyst. At the same time, the C_2 -dimers cease from reaction products.

The trends associated with different catalyst screening protocol (downward or upward variations in P_{H_2}) are collected in Fig. 2. They indicate large changes associated with the catalyst deactivation, accompanied by downward changes of P_{H_2} or catalyst reactivation, when the hydrogen pressure was increased. We believe that the much better catalytic behavior of the catalyst samples which were first subjected to hydrogen-richer reaction conditions results from a kind of catalyst activation. At very high CCl_4 conversion, when only negligible amounts of C_2 -dimeric species are formed, huge amounts of HCl (inevitable HdCl product) and hydrogen (reactant in excess), must interact with the catalyst surface rendering it more suitable for this reaction. In this respect it should be noted that a considerable induction period in the HdCl behavior of Pt/MgO catalyst disappeared when reaction was conducted after Pt/MgO had been pretreated with 18 % HCl- H_2 gas and reduced with hydrogen at 573 K for 2 h [12]. Kim et al. [12] regard a Pt(II) species as a dominant active species. Recent Dow Chemical Company patent [13] also includes the HCl + H_2 pretreatment in activation procedure of CCl_4

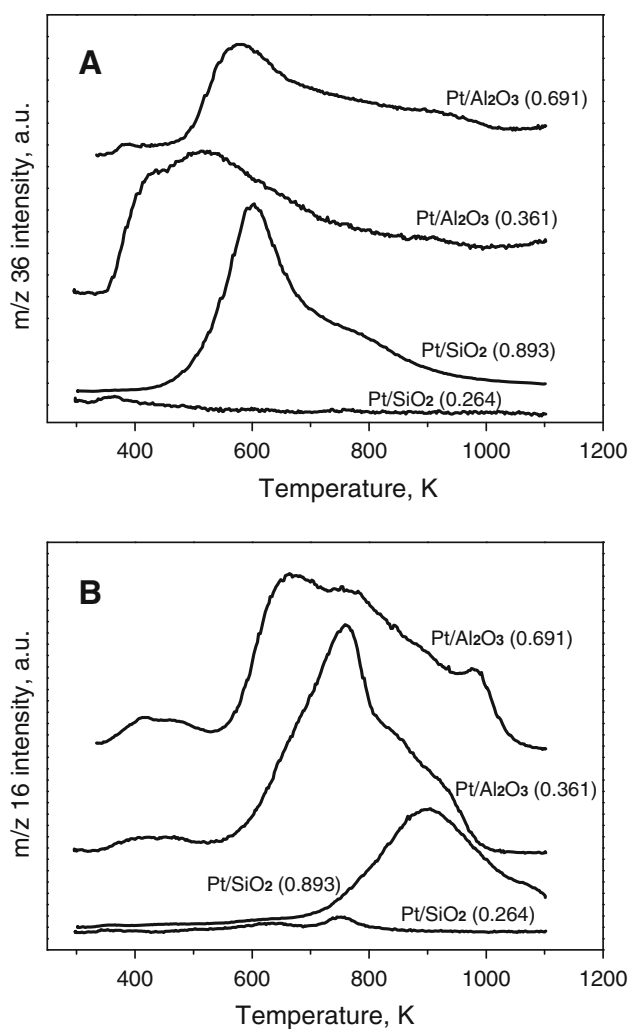


Fig. 4 TPH of post-reaction deposits. **a** Evolution of HCl, **b** evolution of methane

HdCl catalysts. We have also tested the effect of catalyst's pretreatment with HCl. To this aim, the experiment with A1 catalyst pretreated with CCl_4 and H_2 (described in subsection 2.2, HCl was produced in situ from CCl_4), at 363 K for 2 h resulted in an improvement of catalytic behavior (expressed as a single star in upper section of Fig. 2). It must be stressed that although our conditions of catalyst's chloriding were much milder than those in [12, 13], the effect of this pretreatment substantiates the speculations as to the beneficial role of the catalyst's screening protocol starting from hydrogen-rich conditions.

It appeared clear from the foregoing that the search for the effect of hydrogen partial pressure on the catalytic behavior should be realized by catalyst screening at a gradually descending H_2/CCl_4 ratio. Results of such studies are shown in Fig. 3, presented as $\log(\text{conversion}) - \log(P_{\text{H}_2})$ relations, just to check if one has a direct insight into

the reaction order in hydrogen. Different situations were found for various platinum catalysts. The highly dispersed catalysts (A1 and, especially, S1) showed nearly full conversion at the reaction temperature 363 K, at P_{H_2} between 30.1 and 96.9 kPa. Such very high conversion levels preclude assessment of real reaction orders. The numbers showed in a few cases (n_{H} 's, from line slopes) in Fig. 3 serve only as an indication of a linear character of certain correlations. Very low apparent activation energies found for hydrogen-rich conditions do not also reflect the real reaction kinetics. In this respect, more realistic is the kinetic data collected for catalyst A1 (and A6) at lower reaction temperatures, i.e. at 343 and 353 K: n_{H} values are close to $\frac{1}{2}$, i.e. suggestive of the participation of dissociated hydrogen [14, 15]. It is also easy to notice an abrupt decrease of the overall conversion when the P_{H_2} is changed from 30.1 to ~ 21 kPa. But in this case, the n_{H} values higher than 5 (for A1) and 2 (for S1) indicate that under hydrogen deficient conditions, both Pt catalysts with high dispersion are deactivated. On the other hand, the apparent activation energies for A1 and S1 catalysts collected at hydrogen-poor conditions are close to the respective values reported in the literature [1, 3, 14].

In other cases it is impossible to draw straight line relations (Fig. 3, A9, S8, S11). For less metal dispersed Pt/SiO₂ catalysts (Fig. 3, S8, S11), the respective log–log relations possess maxima. This may suggest that CCl_4 HdCl undergoes via a Langmuir–Hinshelwood mechanism [16], when both reactants (CCl_4 and H_2 , in our case) compete for active surface sites. Similar mechanism was earlier suggested to operate in HdCl of dichlorodifluoromethane over supported Pd catalysts [17]. It should also be recalled that so-called volcano- (or bell-) shaped relations between catalytic activity and hydrogen pressure were frequently reported and interpreted for alkane catalytic hydroconversions (hydrogenolysis, isomerization or dehydrocyclization) on unsupported and supported platinum catalysts [18–20]. Paál [21] demonstrated that hydrogen coverage effects in alkane catalytic conversion would lead to a drastic decrease of activation energy, resulting even in inverse Arrhenius plots. Such effects would also operate in catalytic HdCl, although the present results obtained at very highly conversion level render a more detailed discussion difficult. However, it must be emphasized that in the case of S8 and S11 catalysts, which exhibited maxima in the conversion- H_2 pressure relations, the apparent activation energies were found roughly between 27 and 36 kJ/mol, not much dependent on the H_2 pressure.

In order to decide between poisoning effects of deposited chlorine/chloride species and carbonaceous residues, the TPH runs appears helpful in showing how to eliminate chlorine from a catalyst without a considerable removal of

carbon. The 1.5 wt% Pt/Al₂O₃ and Pt/SiO₂ catalysts used in CCl₄ HdCl showed the maximum of chlorine removal rate by hydrogen at the temperature below 600 K (Fig. 4a). For the alumina-supported catalysts a pronounced tail in HCl trace developed at higher temperatures suggests evolution from the support. Carbon-containing species leave (as methane) all tested catalysts at much higher temperatures. Therefore these carbonaceous deposits should be regarded as most effective active site blockers, in agreement with others [5, 6, 8, 22]. Very low amounts of desorbed HCl and CH₄ from a medium-dispersed Pd/SiO₂ catalyst (S8, fraction exposed [FE] = 0.264, Fig. 4a, b) are in good agreement with our earlier report [1], where Fig. 2 (on p. 252) also shows rather small amounts of liberated HCl and methane from catalyst S5 (FE = 0.377, not tested in the present study). Both the low platinum dispersion and the fact of using silica support appear to rationalize such a behavior, and, in effect, much less marked than in the case of alumina-supported counterparts, catalyst's deactivation.

4 Conclusions

Two series of silica- and alumina-supported platinum catalysts were investigated in the HdCl of tetrachloromethane at the reaction temperature range 343–363 K, at different H₂/CCl₄ ratios and very short contact times (≤ 0.26 s). During an initial period of reaction carried out at a lower H₂/CCl₄ ratio (6.7 and less), all catalysts deactivated with time-on-stream, the effect was more drastic for highly dispersed Pt catalysts. After a long-term screening and reaching a steady state, the increase of H₂/CCl₄ ratio to 13.4 brought about significant changes in the catalytic behavior. In particular, this effect was remarkable for the Pt catalysts characterized by the highest metal dispersions, for which the overall conversion rate was increased by an order of magnitude and the selectivity to chloroform raised from ~60 to ~90 %. Such impressive activity growth cannot be explained by a positive reaction order in hydrogen, the more so as this variation was not immediate but it was progressively developed with time-on-stream. It seems that during the initial reaction period at the lower H₂/CCl₄ ratio, the catalysts quickly deactivated by unreactive deposits, but at a higher hydrogen pressure these deposits were gradually removed, making the surface of platinum active and selective towards chloroform. A prolonged catalyst screening carried out with gradually decreasing H₂/CCl₄ ratios (from 21.7 to 6.7, and less) resulted in much better catalyst's performance than it was observed for the reversed order of H₂/CCl₄ ratio. It appears that the catalysts subjected to hydrogen-rich reaction conditions are better activated, probably because of the action

of an intense HCl flux, generated in the reaction. Because of a very high activity of a few tested samples, changes of CCl₄ conversion with the hydrogen partial pressure do not reflect real reaction orders in hydrogen. The same reason may lead to falsification of apparent activation energy. In other cases the relation between conversion and hydrogen pressure shows maxima, suggesting that HdCl undergoes via a Langmuir–Hinshelwood mechanism, when hydrogen and CCl₄ compete for metal surface sites. Both carbon- and chlorine-containing deposits were found in the post-reaction catalyst samples.

Acknowledgments This work was supported by the Polish Ministry of Science and Higher Education within Research Project N N204 161636.

Open Access This article is distributed under the terms of the Creative Commons Attribution License which permits any use, distribution, and reproduction in any medium, provided the original author(s) and the source are credited.

References

- Bonarowska M, Kaszukur Z, Kępiński L, Karpiński Z (2010) Appl Catal B 99:248
- Zhang ZC, Beard BC (1999) Appl Catal A 188:229
- Prati L, Rossi M (1999) Appl Catal B 23:135
- Legawiec-Jarzyna M, Juszczyk W, Bonarowska M, Kaszukur Z, Kępiński L, Kowalczyk Z, Karpiński Z (2009) Top Catal 52:1037
- Choi HC, Choi SH, Lee JS, Lee KH, Kim YG (1997) J Catal 166:284
- Bae JW, Park ED, Lee JS, Lee KH, Kim YG, Yeon SH, Sung BH (2001) Appl Catal A 217:79
- Dal Santo V, Dossi C, Recchia S, Colavita PE, Vlaic G, Psaro R (2002) J Mol Catal A 182–183:157
- Bae JW, Lee JS, Lee KH (2008) Appl Catal A 334:156
- Bernard P-M, Primet M (1990) J Chem Soc Faraday Trans 86:567
- Guczi L, Karpiński Z (1979) J Catal 56:438
- McKee DW, Norton FJ (1964) J Catal 3:252
- Kim SY, Choi HC, Yang B, Lee KH, Lee JS, Kim YG (1995) J Chem Soc Chem Commun 21:2169
- Holbrook MT, Myers JD US Patent 2007/0225530 A1 (Publication date: 2007-09-27) (to the Dow Chemical Company)
- Weiss AH, Gambhir BS, Leon RB (1971) J Catal 22:245
- Thompson CD, Rioux RM, Chen N, Ribeiro FH (2000) J Phys Chem B 104:3067
- Bond GC, Hooper AD, Slaa JC, Taylor AO (1996) J Catal 163:319
- Coq B, Cognion JM, Figuéras F, Tourmigant D (1993) J Catal 141:21
- Paál Z (1980) Adv Catal 29:273
- Paál Z (1992) Catal Today 12:297
- Wootsch A, Paál Z (2002) J Catal 205:86
- Paál Z (1985) J Catal 91:181
- Frankel KA, Jang BW-L, Roberts GW, Spivey JJ (2001) Appl Catal A 209:401
- Rachmady W, Vannice MA (2000) J Catal 192:322