

Hydrodechlorination of dichlorodifluoromethane, carbon tetrachloride and 1,2-dichloroethane over Pt/Al₂O₃ catalysts

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Abstract

A comparative study of hydrodechlorination of dichlorodifluoromethane, carbon tetrachloride and 1,2-dichloroethane over alumina-supported Pt catalysts showed several interesting features in the catalytic behavior. Platinum proved to be very good catalyst in CCl₄ hydrodechlorination (with high selectivity toward CHCl₃), whereas for CCl₂F₂ and 1,2-dichloroethane hydrodechlorinations this metal exhibits rather low activity and, in addition, converts the reactants to less valuable products (e.g. alkanes). However, a rapid deactivation of Pt catalysts during hydrodechlorination requires their frequent regeneration. Two regeneration protocols tested in this work showed interesting, albeit somewhat different, activity evolutions. Removal of chlorine species by hydrogen at 350 °C led to a moderate increase of catalytic activity. On the other hand, a partial removal of carbonaceous residues by oxidative pretreatment brought about a considerable increase of the overall conversion level in CCl₄ hydrodechlorination. Additional temperature-programmed experiments with spent and regenerated Pt/Al₂O₃ catalyst suggest that a partial removal of carbonaceous deposit (most probably followed by its reconstruction) leading to the formation of very active catalyst, less susceptible to poisoning by chlorine.

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1. Introduction

Catalytic hydrodechlorination of organic wastes containing a variety of harmful and ozone-depleting compounds has recently attracted increasing interest [1,2]. Several catalysts were tested in fundamental studies, and then proposed in patent applications (references in [3]). Among the catalytic metals, platinum and palladium seem to play the most important role in chlorine removal from organic molecules [4–21]. Supported on various carriers (like active carbon, alumina, AlF₃, silica, magnesia, etc.), Pt and Pd appeared very effective in chlorine elimination from CFCs and chloroalkanes. One has, nevertheless, to note some differences in the

catalytic behavior of these metals. Whereas Pd is a unique catalyst in the selective hydrodechlorination of chlorofluorocarbons (CFCs) to hydrofluorocarbons (HFCs) [4], Pt seems a better catalyst in a gas phase hydrodechlorination of carbon tetrachloride to chloroform [5,8,12]. Apart from variations in the selectivity, these metals often exhibit different durability. For example, palladium catalysts show a rather short lifetime in carbon tetrachloride hydrodechlorination carried out in the gas phase [12].

Recently, we have compared the hydrodechlorination of several chlorine-containing compounds (CCl₂F₂, CCl₄ and ClCH₂–CH₂Cl) over alumina-supported Pt–Pd catalysts [22]. A number of synergistic effects were found, e.g. an addition of platinum to 1 wt.% Pd/Al₂O₃ catalyst brought about interesting changes in the activity and selectivity in hydrodechlorination of CCl₂F₂ and 1,2-dichloroethane

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[22]. In addition, an attempt to elucidate catalyst's deactivation (the effect often found in catalytic transformation of CCl_4) was undertaken. Coke and chlorine deposition were considered as the main possible reasons of deactivation, assuming after others [5,16] that changes in metal dispersion (in alumina-supported metals, like Pt) during hydrodechlorination are not large. In our previous work [22], one Pd-Pt/ Al_2O_3 catalyst was subjected to a few chlorine removal operations during its screening in CCl_4 reaction. It appeared that after chlorine removal by hydrogen treatment at 350°C the overall conversion of CCl_4 quickly returned to a steady-state level exhibited before chlorine elimination. Such a result indicated that the main reason of a continuous deactivation is the formation of carbonaceous species, and not a metal surface chloriding. However, important changes in the selectivity toward CHCl_3 , generated by short reduction periods, suggested that, although the overall activity is largely determined by the amount of deposited carbonaceous material, nevertheless the reduction of a coked catalyst may result in some reconstruction of carbonaceous residues [22], contributing to significant selectivity changes. In order to avoid any complications with an additional factor associated with possible changes in the surface composition of bimetallic Pd-Pt catalyst, we decided to reinvestigate the problem of catalyst's deactivation and regeneration by focusing our attention at the monometallic Pt/ Al_2O_3 catalyst.

2. Experimental

2.1. Catalyst preparation and characterization

The 1 wt.% metal-loaded platinum catalyst was prepared by incipient wetness impregnation of alumina (Alumina Catalyst Shell S618, $240\text{ m}^2/\text{g}$, pore volume $0.8\text{ cm}^3/\text{g}$, 75–120 mesh, acid washed and precalcined at 550°C) with an aqueous solution of chloroplatinic acid. Before impregnation the support was dried in an air oven at 100°C for 20 h. H_2PtCl_6 was prepared by dissolving Pt wire (Johnson Matthey Grade 1) in a hot mixture of hydrochloric and nitric acids (volume ratio 10:1, both of analytical purity from POCh, Gliwice, Poland). 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 90°C .

The prepared catalyst was reduced in flowing 85% H_2/Ar ($25\text{ cm}^3/\text{min}$), ramping the temperature from 20 to 400°C (at $8^\circ\text{C}/\text{min}$) and kept at 400°C for 3 h. After a subsequent purge in argon flow at 400°C for 1 h, the catalyst was characterized by H_2 chemisorption. Hydrogen chemisorption experiment was performed in a pulse-flow system, and showed the fraction exposed of platinum equal 0.54 (as H/Pt). All the gases used (H_2 , Ar and 85% H_2/Ar mixture) were purified

by passing through drying traps with final purification over MnO/SiO_2 .

2.2. Catalytic tests

The reactions of hydrodechlorination of 1,2-dichloroethane, carbon tetrachloride and dichlorodifluoromethane were carried out at atmospheric pressure, in glass flow reactors equipped with fritted disks to place a catalyst charge. Prior to reactions, the catalyst was reduced in flowing 10% H_2/Ar ($25\text{ cm}^3/\text{min}$), ramping the temperature from 20 to 400°C (at $8^\circ\text{C}/\text{min}$) and kept at 400°C for 3 h. All reactions were followed by gas chromatography (HP 5890 series II with FID, a 5% Fluorcol/Carbopack B column (10 ft) from Supelco).

In the catalytic conversion of 1,2-dichloroethane (HPLC grade, 99.8% pure from Sigma-Aldrich, Germany) the flows of all gases, except 1,2-dichloroethane, were fixed by using Bronkhorst Hi-Tec mass flow controllers. After reduction, the catalyst was cooled to 200°C , then contacted with the reaction mixture, i.e. with a flow of hydrogen + argon at $41.2\text{ cm}^3/\text{min}$ and 1,2-dichloroethane, provided from a saturator kept at 0°C (to give the partial pressure of 1,2-dichloroethane of 2.9 kPa). The partial pressure ratio $P_{\text{H}_2}/P_{\text{C}_2\text{H}_4\text{Cl}_2}$ was 1:1.

The mass of catalyst used ranged between 0.1 and 0.4 g, depending on the reaction, in order to not exceed conversion levels beyond 10% (at steady state, for freshly reduced samples). In all kinetic runs, the activities of most catalysts declined with time-on-stream. A typical run lasted ~ 24 h.

A similar reaction protocol was adopted for CCl_4 and CCl_2F_2 hydrodechlorinations. CCl_4 (analytical reagent from POCh, Gliwice, Poland, purity $>99.6\%$) was fed in the same fashion as 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$, i.e. from a saturator kept at 0°C , whereas in the case of CCl_2F_2 , the reactant was supplied from a gas tank (Galco S.A., Belgium; purity 99.9%). 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. Hydrogen and argon were purified by MnO/SiO_2 , and the overall flow rate of the reactant gas mixture was $100\text{ cm}^3/\text{min}$. In the case of CCl_4 hydrodechlorination the CCl_4/H_2 ratio was 1:7 (with the total flow of $\sim 29\text{ cm}^3/\text{min}$).

Blank experiments with alumina showed very low activity in the temperature range used for screening Pt/ Al_2O_3 catalyst, i.e. 200°C for 1,2- $\text{C}_2\text{H}_4\text{Cl}_2$, 180°C for CCl_2F_2 , and 90°C for CCl_4 hydrodechlorinations.

After reaction, some samples of used Pt/ Al_2O_3 catalyst were subjected to temperature-programmed hydrogenation (TPH, next subsection). Obtained TPH spectra allowed us to propose two regeneration scenarios: one by hydrogen, the other by oxygen treatment at 350°C . More details on these procedures are provided in Section 3.

2.3. Temperature-programmed hydrogenation (TPH) and temperature-programmed oxidation (TPO) of used Pt/Al₂O₃ catalysts

After kinetic runs the catalysts were investigated by a temperature-programmed hydrogenation (TPH) to detect species which can be removed by hydrogen from used catalysts. Progress of TPH runs, using a 10% H₂/He flow (25 cm³/min) at a 10 °C/min ramp, was followed by mass spectrometry (MA200, Dycor-Ametek, Pittsburgh). Several masses were monitored during the experiment, but major changes were seen only for *m/z* 15 and 16 (methane evolution). Attention was also focused at changes in *m/z* 36 and 38, which are suggestive of HCl liberation from used catalysts. Evolution of hydrogen pressure (*m/z* 2) showed that desorption of chlorine needed hydrogen from the gas phase. Only the results of testing the catalysts after CCl₂F₂ and CCl₄ reactions were analyzed. In a similar fashion, a few temperature-programmed oxidation (TPO) runs were performed to estimate relative amounts of coke deposited on the Pt/Al₂O₃ catalyst after CCl₄ hydrodechlorination and a similar spent sample which was subsequently regenerated in an oxidizing atmosphere at 350 °C. To this end, a 1% O₂/He flow (25 cm³/min) at a 10 °C/min ramp, was followed by mass spectrometry, with particular attention paid to *m/z* 44 (CO₂ evolution) and *m/z* 32 (O₂ consumption).

3. Results and discussion

All catalysts showed a marked deactivation during the initial period of reaction. Steady-state data (typical results presented in Table 1) were used for further interpretation. It is seen that the reaction of CCl₄ proceeds much faster than the remaining reactions (CCl₂F₂ and 1,2-dichloroethane hydrodechlorinations), in accordance with a much higher reactivity of CCl₄ molecule. For CCl₄ reaction one notes a respectable level of the selectivity toward chloroform (almost 90%), which is a typical feature of platinum-based catalysts. For the other reactions, the overall activity of Pt/Al₂O₃ is low, at least for the temperatures, at which palladium-based catalysts show a higher conversion. In addition, a good prod-

uct selectivity typical for palladium catalysts was not obtained with the Pt/Al₂O₃: only very small amounts of desirable products (CH₂F₂ from CCl₂F₂, and ethene from 1,2-dichloroethane) were received. Instead, very high selectivities to either methane (from CCl₂F₂) or ethane (from 1,2-dichloroethane) were displayed (Table 1). These results and relatively small changes in the catalytic behavior of Pt/Al₂O₃ catalysts in the above-mentioned reactions prompted us to focus our attention mainly at the CCl₄ reaction.

The steady-state behavior of Pt/Al₂O₃ catalysts in hydrodechlorination is associated with the degree of catalyst's deactivation during reaction. Following other published results [15,23,24], we consider that deactivation would be caused by blocking active sites by surface chlorine and/or carbonaceous residues. According to other works [5,16] rather negligible platinum sintering takes place during hydrodechlorination at a relatively low reaction temperature (90–200 °C), so this factor is not considered in this work. In order to decide between poisoning effects of deposited chlorine/chloride species and carbonaceous residues, the temperature programmed hydrogenation runs (TPH) appears helpful in showing how to eliminate chlorine from a catalyst without a considerable removal of carbon. The 1 wt.% Pt/Al₂O₃ catalyst used in CCl₄ hydrodechlorination shows the maximum of chlorine removal rate by hydrogen at the temperature below 300 °C (Fig. 1, thick line). Simultaneously, methane liberation from the same sample commences at much higher temperature (maximum rate at 550–600 °C, Fig. 2). This information led us to the first type of catalyst regeneration by hydrogen treatment at 350 °C (only chlorine removal, without affecting a carbon-containing deposit, vide infra). Carbon removal by hydrogen treatment appeared not acceptable, because very high temperature needed for this process (~600 °C, Fig. 2) would cause a considerable metal sintering. To this end, the other type of regeneration, relied on a short oxidative treatment of a spent catalyst in the oxidative atmosphere at 350 °C was used (for details of regeneration procedures, see caption to Table 2). This temperature level was chosen on the basis of a recent paper by Choi et al. [16], where temperature programmed oxidation of coke from Pt/Al₂O₃ catalysts used in CCl₄ hydrodechlorination was investigated (Figs. 3 and 4 in Ref. [16]). According to

Table 1
Representative kinetic data of hydrodechlorination over 1 wt.% Pt/Al₂O₃ catalyst: product selectivities and turnover frequencies

Product selectivity (%)	Turnover frequency ^a (s ⁻¹)
CCl ₂ F ₂ hydrodechlorination at 180 °C ^b CH ₄ : 56, CH ₂ F ₂ : 9, CClF ₃ : 0.5, CH ₃ Cl: 7, CHClF ₂ : 28, CH ₂ ClF: –	0.0007
CCl ₄ hydrodechlorination at 90 °C CH ₄ : 11.1, C ₂ H ₄ + C ₂ H ₆ : 0.5, C ₃ H ₆ + C ₃ H ₈ : –, C ₄ ^c : –, CHCl ₃ : 88.4	0.0200
ClCH ₂ –CH ₂ Cl hydrodechlorination at 200 °C ^d CH ₄ : 1.2, C ₂ H ₄ : 0.1, C ₂ H ₆ : 84.6, C ₂ H ₅ Cl: 3.1, 1,2-C ₂ H ₂ Cl ₂ : 9.4	0.0066

^a Assuming metal fraction exposed measured by H₂ chemisorption (H/Pt = 0.54).

^b Other minor products: CHF₃, C₂H₆, CH₂Cl₂.

^c Higher hydrocarbons and chlorohydrocarbons.

^d Other minor products: C₂H₃Cl, C₃H₈, C₄H₁₀.

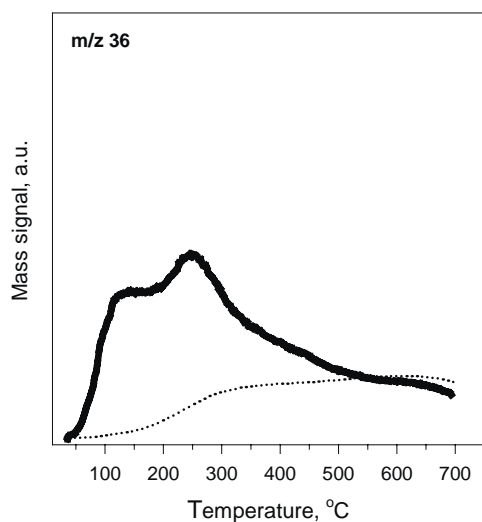


Fig. 1. HCl (as m/z 36) evolution during temperature-programmed hydrogenation of Pt/Al₂O₃ catalysts used in CCl₄ reaction. Thick line—after reaction on freshly reduced catalyst, dotted line—after reaction on the catalyst subjected to regeneration in an oxidizing atmosphere at 350 °C. Comparable catalyst weights (~0.1 g) were used.

the TPH spectrum, the oxidative regeneration results in a drastic reduction of chlorine retention by the catalyst during CCl₄ hydrodechlorination (Fig. 1, dotted versus thick line). A nearly common course of both TPH profiles (Fig. 1) at very high temperatures (i.e. >500 °C) suggests that some part of the deposited chlorine must also originate from alumina. On the other hand, a relatively small amount of chlorine removable by TPH at lower temperatures for the Pt/Al₂O₃ catalyst regenerated in the oxidative atmosphere indicates that this type of regeneration does not restore an initial form of the metal surface.

Catalytic results of various regeneration procedures showed very interesting changes, especially for the samples regenerated in the oxidative atmosphere. A remarkable activity growth in CCl₄ hydrodechlorination (see below) was

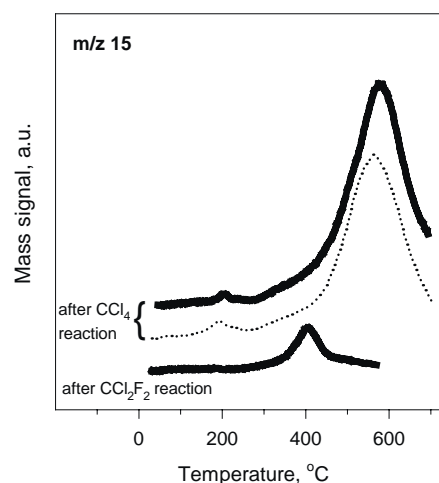


Fig. 2. Methane evolution during temperature-programmed hydrogenation of used Pt/Al₂O₃ catalysts after hydrodechlorination of CCl₂F₂ and CCl₄ thick line—for the freshly reduced catalyst; dotted line—for the catalyst subjected to regeneration in an oxidizing atmosphere at 350 °C. Mass 15 was selected for presentation because CH₄ liberation observed by monitoring mass 16 is somewhat misinterpreted due to evolution of water (especially around 100 °C). Comparable catalyst weights (~0.1 g) were used.

associated with a partial (i.e. not complete) removal of carbon from the catalyst. Our belief, implied by visual inspection of the catalyst after oxidative regeneration (remained greyish, not nearly white), is substantiated by comparing the result of temperature-programmed oxidation (TPO) study of the sample of Pt/Al₂O₃ after reaction with that after reaction and a consecutive regeneration in an oxidative atmosphere at 350 °C (Fig. 3). The amount of carbon released as CO₂ from the catalyst after regeneration is nearly two times smaller than the analogous quantity of C from the spent catalyst.

The results of various regeneration procedures are shown in Figs. 4–6 (time-on-stream behavior) and Table 2 (steady-state data). First, the Pt/Al₂O₃ catalyst was subjected to a few chlorine removal operations during its screening in CCl₄

Table 2
The effect of various regenerative pretreatments

Reaction (sample)	Catalyst weight (g)	Steady-state conversion (%) after:		
		Reduction ^a	Regeneration #1	Regeneration #2
CCl ₂ F ₂ reaction at 180 °C				
Two regenerations in H ₂ only ^b	0.201	0.19	0.15	0.17
Two O ₂ /H ₂ regenerations ^c (#1, #2)	0.368	0.40	0.23	0.22
CCl ₄ reaction at 90 °C				
Two regenerations in H ₂ only	0.106	2.69	12.1	10.8
Two O ₂ /H ₂ regenerations (#1, #2)	0.101	2.97	61.1	69.6
ClCH ₂ –CH ₂ Cl reaction at 200 °C				
Two regenerations in H ₂ only	0.158	3.90	6.93	10.5
Two O ₂ /H ₂ regenerations (#1, #2)	0.151	2.94	8.74	16.2

Steady-state conversions in the reaction of CCl₂F₂, CCl₄ and 1,2-dichloroethane hydrodechlorination over 1 wt.% Pt/Al₂O₃ catalyst.

^a Steady-state conversions on a freshly reduced (at 400 °C) 1 wt.% Pd/Al₂O₃ (see Section 2).

^b Steady-state conversions on 1 wt.% Pt/Al₂O₃ subjected to regeneration in hydrogen at 350 °C (see caption to Fig. 4).

^c Steady-state conversion on used 1 wt.% Pt/Al₂O₃ (after Footnote b) subjected to regeneration in an oxidative atmosphere at 350 °C, followed by rereduction in hydrogen at 350 °C (see caption to Fig. 5).

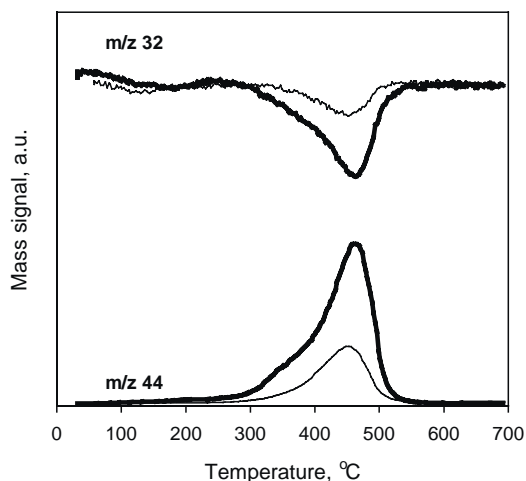


Fig. 3. TPO of coke from 1 wt.% Pt/Al₂O₃: thick line—after CCl₄ hydrodechlorination at 90 °C, thin line—after CCl₄ hydrodechlorination at 90 °C and subsequent regeneration in an oxidizing atmosphere at 350 °C (for details see text). Comparable catalyst weights (~0.1 g) were used.

reaction. Fig. 4 shows the results. It appears that after regeneration in H₂ and returning the flow of reaction mixture, the overall conversion at steady-state exceeds the level exhibited before regeneration in H₂, by factor of ~4. However, this type of regeneration does not introduce large changes in the selectivity (small decrease of S_{CHCl₃}). Such a beneficial change in the catalytic behavior suggests that, although the overall activity seems still be largely determined by the amount of deposited carbonaceous material, nevertheless the rereduction of a coked catalyst may result in some reconstruction of the carbonaceous residues.

The oxidative type of catalyst regeneration (at 350 °C) brings about much more interesting changes in the catalytic behavior. Fig. 5 and Table 2 show that after regeneration, the overall conversion level grows by factor of >20. As it has already been mentioned this remarkable activity growth would be associated with a partial (i.e. not complete) removal of

carbon from the catalyst. We hypothesize that a considerable reconstruction of the carbonaceous deposit, much more effective than that obtained by regeneration in H₂, must occur during coke oxidation. It is believed that CCl₄ bonding to such a modified Pt surface is weaker, leading to a higher turnover efficiency. Additional TPH experiments with the catalyst regenerated in the oxidizing atmosphere at 350 °C (Figs. 1 and 2) suggest that the improvement of the catalytic performance after regeneration is associated with its better resistance to poisoning by chlorine/chloride species (Fig. 1). In line with this suggestion, Zhang and Beard [7,9] showed that the main reason of catalyst's poisoning in this reaction is chlorine/chloride deposition, more distinct for highly (than poorly) dispersed Pt catalysts. Regeneration in the oxidative atmosphere at 350 °C of the Pt/Al₂O₃ clearly results in a very much diminished deposition of chlorine species (Fig. 1), especially of those which are removable by hydrogen at lower temperatures (<350 °C). It is assumed that the presence of larger amounts of chlorine on platinum surface during hydrodechlorination is the cause of a reduced catalytic activity of platinum.

TPH experiments indicate that the catalyst's regeneration in the oxidative atmosphere at 350 °C does not result in a considerable reduction of carbonaceous species deposited on the catalyst during reaction (dotted versus solid line in Fig. 2). Therefore, the beneficial role of a reconstructed carbonaceous deposit (after oxidative regeneration) must be seen in a considerable resistance to chlorine poisoning.

Fig. 6 shows the effect of temperature used in oxidative regeneration of 1 wt.% Pt/Al₂O₃. After first oxidative regeneration performed at 350 °C (as above), the second regeneration run was carried out at 400 °C, in belief that coke burning from this catalyst should be more complete at this temperature. The overall conversion decreased from a higher value characteristic for a "350 °C" type of regeneration (~60%) to a much lower level, typical for a freshly reduced catalyst. It is also evident that the level of conversion grows steadily

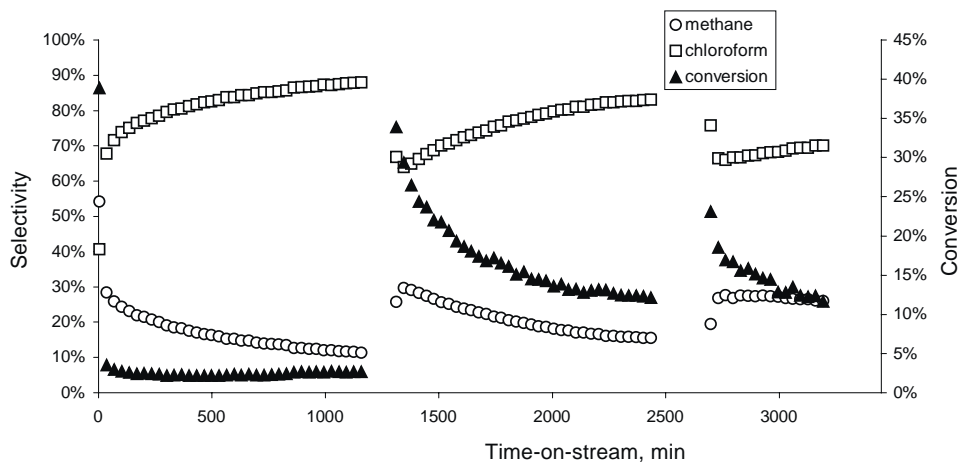


Fig. 4. CCl₄ hydrodechlorination on 1 wt.% Pt/Al₂O₃ (mass ~0.1 g) at 90 °C. Breaks in the trace indicate two short regeneration pretreatments in hydrogen at 350 °C. Regeneration pretreatment: heating the catalyst from 90 °C to 350 °C in 10% H₂/Ar flow (25 cm³/min) at a 10 °C/min ramp, then cool-down to 90 °C (reaction temperature).

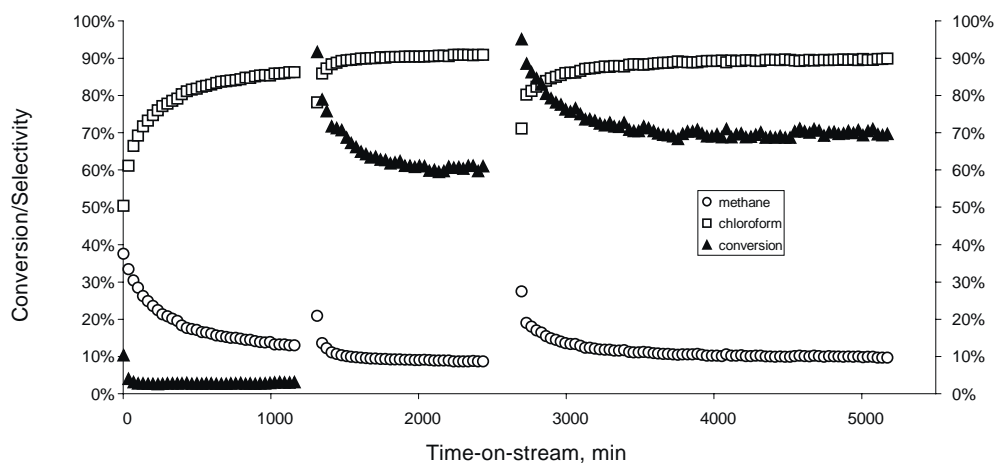


Fig. 5. CCl_4 hydrodechlorination on 1 wt.% $\text{Pt}/\text{Al}_2\text{O}_3$ (mass ~ 0.1 g) at 90°C . Breaks in the trace indicate two short regeneration pretreatments in oxygen at 350°C . Regeneration: heating the catalyst from 90°C to 350°C in 10% H_2/Ar flow ($25\text{ cm}^3/\text{min}$) at a $10^\circ\text{C}/\text{min}$ ramp, then a short purge in Ar, next 5% O_2/Ar flow ($25\text{ cm}^3/\text{min}$) at 350°C for 30 min, then H_2/Ar flow at 350°C and cool-down to 90°C .

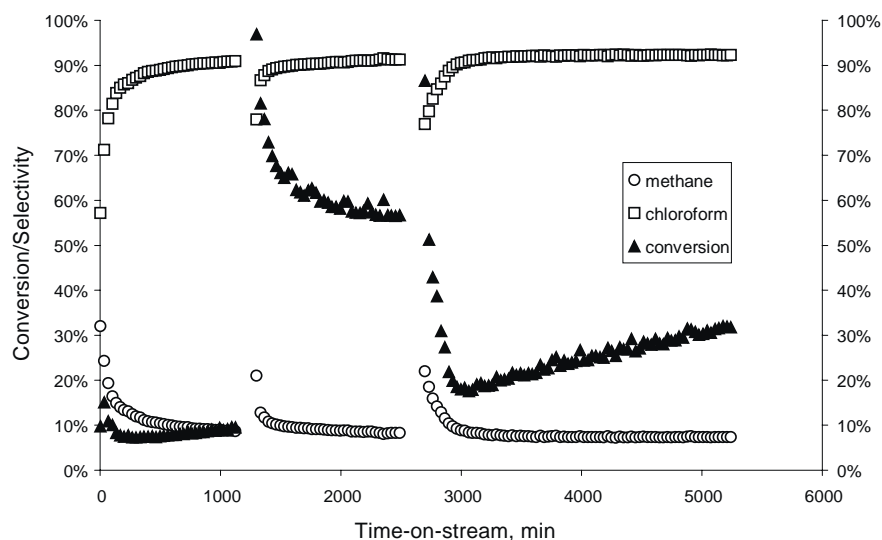


Fig. 6. CCl_4 hydrodechlorination on 1 wt.% $\text{Pt}/\text{Al}_2\text{O}_3$ (mass ~ 0.1 g) at 90°C . Breaks in the trace indicate two short regeneration pretreatments: first in O_2/Ar at 350°C , then in O_2/Ar at 400°C , both oxidations followed by short reduction periods.

with time-on-stream, in line with the behavior of the fresh catalyst. Thus, it is considered that the oxidative regeneration at 400°C is sufficient to remove a predominant amount of carbonaceous residues from used $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst.

It should be mentioned that TPH after CCl_2F_2 reaction revealed only minute amounts of chlorine in used $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts (TPH trace not shown). Similarly, rather small amounts of carbon were deposited after reaction (Fig. 2). Therefore, the regenerative procedures of $\text{Pt}/\text{Al}_2\text{O}_3$ would not lead to large changes in catalytic behavior (Table 2). In the case of 1,2-dichloroethane reaction, the respective changes in activity generated by the oxidative regeneration are more marked than for CCl_2F_2 conversion, and similar in nature as for CCl_4 reaction (a several times increase of conversion, Table 2), without large change in product selectivity (not shown).

Summing up, it is concluded that after CCl_4 reaction regeneration of a coked $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst by oxidation at

350°C results in the beneficial reconstruction of the carbonaceous residues. It seems possible that changes in the structure of coke would lead to the formation of a variety of active sites associated with a different degree of steric constraints, and contribute to considerable activity changes. The presence of different active centers related to specific sites in the coke structure has recently been proposed by Borodziński [25,26] in his mechanism of selective hydrogenation of acetylene on palladium catalysts.

4. Conclusions

A comparative study of hydrodechlorination of CCl_2F_2 , CCl_4 and $\text{ClCH}_2\text{--CH}_2\text{Cl}$ on $\text{Pt}/\text{Al}_2\text{O}_3$ catalysts showed large differences of catalytic behavior. Platinum appeared very efficient catalyst in CCl_4 hydrodechlorination (with high se-

lectivity toward CHCl_3), whereas in case of CCl_2F_2 and 1,2-dichloroethane hydrodechlorinations Pt showed rather low activity and, in addition, converted the reactants to less significant products (e.g. alkanes). However, a rapid deactivation of Pt catalysts during hydrodechlorination always accompanied the reactions. Two types of catalyst regeneration were examined in this work: hydrogenative and oxidative ones. Removal of chlorine species by hydrogen at 350°C led to a moderate increase of catalytic activity. On the other hand, a partial oxidative removal of carbonaceous residues brought about to a huge increase of the overall conversion level in CCl_4 hydrodechlorination (by factor of >20). It is speculated that some forms of reconstructed carbonaceous deposit are beneficial for the reaction, because of a reduced tendency to poisoning by chlorine/chloride species.

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