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Gas-phase hydrodechlorination of dichloromethane with activated carbon-supported metallic catalysts

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ABSTRACT

The deep gas-phase hydrodechlorination (HDC) of dichloromethane (DCM) was studied over several laboratory-made activated carbon-supported metallic catalysts (Pd/C, Pt/C, Ru/C and Rh/C) at atmospheric pressure, reaction temperatures in the 200–250 °C range and space-times of 0.08 and 1.7 kg h mol^{-1}. All the catalysts showed a high activity in HDC of DCM, with conversions in the range 89–99% at the highest temperature and space-time investigated, following the order Rh > Pd > Ru > Pt. Selectivities to non-chlorinated products up to 95% were reached. Methane was the main reaction product in all cases. Hydrodechlorination of DCM with Pt/C catalyst exclusively yielded methane and monochloromethane while hydrocarbons of more than one carbon atom were obtained with the other catalysts. The Pt/C catalyst was highly stable with no loss of activity after 65 h of time on stream at the testing conditions. The deactivation was more pronounced in the case of Ru (DCM conversion decreased a 40% after 20 h of operation), followed by Pd and in a less extent Rh with conversion decreases of 40 and 9%, respectively, after 65 h on stream. The fresh and used catalysts were characterized by N_2 adsorption–desorption, ICP-MS, TPR, XRD, XPS and H_2 and CO chemisorptions. Characterization results suggest that deactivation is mainly related to a decrease of the exposed metallic surface area along the reaction, which appears to be due to poisoning of active centers with chlorinated hydrocarbons, and in the case of Ru/C catalyst also metal sintering.

1. Introduction

Dichloromethane (DCM) plays an important role in the chemical and pharmatheutical industry, where it is used as solvent and reactant. It is also employed in aerosols, adhesives, dry cleaning, etc. [1]. However, because of its high toxicity and carcinogenic character DCM is classified nowadays among the most hazardous gas pollutants [2,3] and is included in the list of the 17 highly harmful chemicals targeted in the emissions reduction effort (33/50 Program) of the U.S. Environmental Protection Agency. Emission of this compound to the atmosphere contributes to the destruction of the ozone layer, to the formation of photochemical smog and to global warming [2–4] and is restricted by strong legal regulations. This enforces the need of developing effective technologies for the treatment of residual streams contaminated with this pollutant. Incineration of wastes containing compounds such as DCM is the most widely used technique but it may lead to more dangerous products than the original contaminants such as phosgene, dioxins and furans. Catalytic hydrodechlorination (HDC) becomes, in this way, one of the most promising emerging technologies. This process has potential economic and environmental advantages over other methods, because it operates at relatively low temperatures and near-ambient pressure and the reaction products are less hazardous than those resulting from other techniques [1,5–7].

It is well known that noble metals are active catalysts for carbon-chlorine bond hydrogenolysis [8,9]. However, there is scarce literature devoted to the hydrodechlorination of dichloromethane, probably due to its lower reactivity when comparing with other organochlorinated compounds (the reactivity of chloromethanes decrease in the order $CCl_4 > CHCl_3 > CH_2Cl_2 > CH_3Cl$ [5,10]), and very few publications use carbon supports. Some references reporting on the deep gas-phase HDC of dichloromethane over different supported metallic catalysts can be found [5,10–16] and only some of them studied this reaction at low concentrations [14–16], which is the most common situation for residual gas effluents. Pd/Al_2O_3 catalysts have been investigated by several authors [11–13], showing low activity in the hydrodechlorination of dichloromethane (<30% at atmospherique pressure, even at 300 °C) though selectivities toward non-chlorinated compounds up to 100% were obtained. Other authors [5,10,17] studied this reaction over several catalysts using different metals and supports, obtaining the best results with Pd and Pt catalysts with conversions near 100% and complete

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dehalogenation. However, in these studies, whether the effect of time on stream is not evaluated or the catalysts are rapidly deactivated. Moreover, the relationship between structure and reactivity is scarcely investigated.

Among the works dealing with chlorinated compounds at low concentrations, Aristizabal et al. [14] and Gonzalez et al. [15,16] reported high activity for Pd/TiO_2 catalysts but they were strongly deactivated. In previous studies of our group, gas-phase hydrodechlorination of dichloromethane with commercial and laboratory-made Pd on activated carbon catalysts were investigated [1,18], with very good results in terms of activity and selectivity to non-chlorinated products. Nevertheless, the catalysts also underwent severe deactivation after few hours of operation, which is a limiting issue regarding technological application.

The causes of deactivation have not been widely investigated and there is not unanimity about that important issue. In the gas-phase operation, deactivation of noble metal catalysts has been linked to HCl/Cl poisoning, formation of carbonaceous deposits, loss of metal through the formation of volatile chlorides, and metal sintering [8,16,19–23]. However, most of these studies do not deal with the hydrodechlorination of chloromethanes and very few publications were referred to activated carbon-supported noble metal catalysts. There is a general agreement on the inhibition of metallic-supported catalysts by the HCl formed in the hydrodechlorination of organochlorinated compounds. However, the use of reactants flowing through a fixed bed reactor avoids local excess of HCl on the catalyst [19], reducing a possible poisoning effect. On the other hand, the nature of the support has been reported to have a significant influence in the poisoning of the catalysts by HCl [14,24]. Ordonez et al. [20] reported a strong poisoning effect of the hydrogen chloride formed in the reaction as well as the formation of carbonaceous deposits as the main causes of deactivation in hydrodechlorination of TTCE with Pd and Pt on activated carbon catalysts. Several authors have proposed the formation of carbonaceous deposits, including chlorine in their constitution in many cases, as one of the main causes of deactivation of these catalysts [16,20,25,26]. Changes in the oxidation state of Pd has also been reported to play a key role in the deactivation of the catalyst in the hydrodechlorination of light organochlorinated compounds over Pd/TiO_2 [16]. In any case, the greatest deactivations have been observed at lowest H_2/organochlorinated ratios and excess hydrogen is needed to minimize coverage by strongly adsorbed species which can block active sites [27,28]. The sintering of metal catalysts appeared to be related to the support. Moon et al. [29] reported the sintering of Pd catalysts on oxide supports as the main cause of deactivation in the gas-phase hydrodechlorination of $CClF_2CF_3$. On the other hand, others authors observed re-dispersion of metal upon hydrodechlorination, but with activated carbon as support [20,25].

In a previous study [18] dealing with the hydrodechlorination of DCM with Pd/C, the catalyst was found to be resistant to metal sintering and HCl poisoning but significant deactivation took place mainly due to the poisoning of active centers with organochlorinated compounds. The aim of this work is testing the activity, selectivity and stability of four laboratory-prepared activated carbon-supported catalysts using Pd, Pt, Rh and Ru as active phase in the hydrodechlorination of dichloromethane. Fresh and used catalysts were characterized by several techniques in order to study the possible causes of catalyst deactivation.

2. Experimental

2.1. Catalyst preparation

Carbon-supported Pd, Pt, Rh and Ru catalysts were prepared by incipient wetness impregnation of a commercial activated carbon supplied by Erkimia S.A. whose characteristics have been reported elsewhere [30]. An aqueous solution containing a precalculated amount of metal salt ($RuCl_3$, $RhCl_3$, $PdCl_2$ and $H_2PtCl_6{\cdot}6H_2O$ supplied by Sigma–Aldrich) adjusted to 1 wt% metal load, was added dropwise to activated carbon while stirring. After drying, activation of all the catalysts was carried out by reduction under continuous H_2 flow. The samples were heated up to 250 °C at a heating rate of 10 °C/min and maintained at this temperature for 2 h. Hydrogen was supplied by Praxair with a minimum purity of 99.999%.

2.2. Catalyst characterization

The porous structure of the catalysts was characterized from the 77 K N_2 adsorption–desorption isotherms using a Quantachrome Autosorb 6B apparatus. The samples were previously outgassed during 4 h at 250 °C and a residual pressure of 10^{-3} Torr.

The bulk metal content was determined via inductively coupled plasma-mass spectroscopy (ICP-MS) in a Perkin-Elmer model Elan 6000 Sciex system that was equipped with an autosampler (Perkin-Elmer model AS-91). The samples were previously digested for 15 min in a microwave oven, using a strongly acid mixture at 180 °C.

Temperature-programmed reduction (TPR) was carried out in a Micromeritics ChemiSorb 2705 pulse analyzer, equipped with TCD detector. Samples of 20 mg were heated at 10 °C/min in a 30 NmL/min flow of 5% H_2 in Ar after they were treated under He (30 Ncm^3/min) at a temperature of 250 °C for 2 h, to clean the catalytic surface. The TPR profiles were registered from 25 to 900 °C.

The X-ray Diffraction patterns of the catalysts and supports were obtained in a X'Pert PRO Panalytical Diffractometer. The powdered sample was scanned using Cu K_α monochromatic radiation ($\lambda = 0.15406$ nm) and a Ge Mono filter. A scanning range of $2\theta = 10^\circ$ to 100° and scan step size of 0.020° with 5 s collection time were used.

The surface of the catalysts was analyzed by X-ray photoelectron spectroscopy (XPS) with a Physical Electronics 5700C Multitechnique System, using Mg Kα radiation ($h\nu = 1253.6$ eV). To determine all the elements present in the catalyst surface, general spectra were recorded for the samples, by scanning up to a binding energy (BE) of 1200 eV. The BE of the Pd $3d_{5/2}$, Pt $4f_{7/2}$, Rh $3d_{5/2}$ and Ru $3d_{5/2}$ core level and full width at half maximum (FWHM) values were used to determine the chemical state of the metal. Correction for binding energies due to sample charging was done by taking the C 1*s* peak (284.6 eV) as an internal standard. The accuracy of the BE scale was ±0.1 eV. The data analysis procedure involved smoothing, a Shirley background subtraction and curve fitting using mixed Gaussian–Lorentzian functions by a least-squares method. Atomic ratios of the elements were calculated from the relative peak areas of the respective core level lines using Wagner sensitivity factors [31].

A Micromeritics ChemiSorb 2705 pulse analyzer was used to measure the catalysts dispersion by CO (Pd/C, Rh/C and Ru/C) or H_2 (Pt/C) chemisorptions at room temperature. The fresh samples (0.15–0.30 g) were first reduced at 250 °C for 2 h under hydrogen flow and then cooled under helium flow (30 Ncm^3/min) at room temperature. Used catalysts (0.15–0.30 g) were previously treated with He (30 Ncm^3/min) at a temperature of 250 °C for 2 h. Several pulses of 50 μL CO or H_2 were then introduced until saturation of the catalyst surface was achieved. The number of exposed metallic atoms was calculated from CO or H_2 chemisorption data. The stoichiometry of the adsorption of CO over the metallic atoms was assumed to be 1 [32–35] and 2 for H_2 [36].

2.3. Catalytic activity

The activity of the catalysts in the hydrodechlorination of dichloromethane was tested in a continuous flow reaction system described elsewhere [1], consisting essentially of a 9.5 mm i.d. fixed bed micro-reactor, coupled to a gas chromatograph with a FID detector for the analysis of the reaction products.

The experiments were performed at atmospheric pressure using a total flow rate of 100 NmL/min, and a H_2/dichloromethane molar ratio of 100. The gas feed, with a dichloromethane concentration of 1000 ppm_v, was prepared by mixing adequate proportions of the starting dichloromethane/N_2 commercial mixture and N_2. The catalyst weight and temperature were adjusted to the desired values in each run. Space-times (τ) of 0.08 and 1.7 kg h mol^{-1} and temperatures of 200–250 °C were tested. To assure the absence of mass transport limitations a series of experiments at 523 K were performed, by modifying the total flow rate and catalyst particle size. No significant changes were found in the DCM conversion values at fixed τ values within the ranges 0.02–0.06 m/s of gas velocity and 0.25–0.71 mm of particle size. The catalysts behavior was evaluated in terms of dichloromethane conversion (X_{DCM}) and selectivities to the different reaction products (S_i). The evolution of the catalytic activity upon time on stream was examined in long-term (65 h) experiments.

The experimental results were reproducible with less than 5% error.

3. Results and discussion

3.1. Characterization of the catalysts

The TPR profiles of the fresh catalysts are shown in Fig. 1. In all cases, there is a maximum in hydrogen consumption at high temperatures (>600 °C), which has been attributed to the interaction of H_2 with reactive surface sites of carbon created by decomposition of functional groups [37,38]. However, the possibility of a metal promoted gasification of the carbon support during TPR cannot be discarded. The palladium catalyst shows a single reduction peak, indicating that this precursor is reduced in one step. The temperature is higher than those found using $PdCl_2$ over other supports [39–41], indicating that the palladium precursor strongly interacts with the activated carbon surface. The H_2 consumption corresponds to the reduction of Pd^{2+} to Pd^0, assuming that palladium is initially present as Pd^{2+}, which is the expected state at the preparation conditions of the catalyst. The TPR profile of Pt/C is similar to those reported in the literature for platinum on amorphous carriers [42–45], which presents a maximum at 245 °C. This peak can be ascribed to the reduction of Pt (II) species to metallic Pt [44]. Rh/C and Ru/C display three peaks of H_2 consumption. The lower temperature peaks (86 and 125 °C for Rh/C and 114 and 184 °C for Ru/C) correspond to the reduction of the metal species similar to those found with other supports when using chlorides as precursors [46], though somewhat displaced to higher temperatures because of a stronger interaction with the carbon surface. The highest reduction temperature peaks (222 °C for Rh/C and 248 °C for Ru/C) cannot be attributed to the presence of big particles since these catalysts show a high dispersion. It can be attributed to metal particles strongly interacted with the support, as it was found by other authors with a Ru/C catalyst prepared from a chloride precursor [47]. These authors ascribed the different interaction of metal particles to the formation of different precursor phases. However, in our case, in the fresh unreduced Rh catalyst only the oxidation state was found by XPS as in the case of Pd and Pt (Figs. 2–4), suggesting that the different interaction is not electronic in nature. In the case of Ru, suitable XPS profiles were not obtained due to the low intensity of the spectra, indicating that the concentration of Ru in the outer surface of the catalyst particles was very low, thus suggesting that Ru is preferentially deposited into the internal pores. The highest reduction temperature peak appears to correspond to metal particles highly interacted in the internal porosity of the catalysts. In fact, most of Ru (which is preferently located in the internal pores of the catalysts as suggested by XPS, presented latter in the text) is reduced at the highest temperatures while most of Rh is reduced at the lowest ones, which denotes a stronger

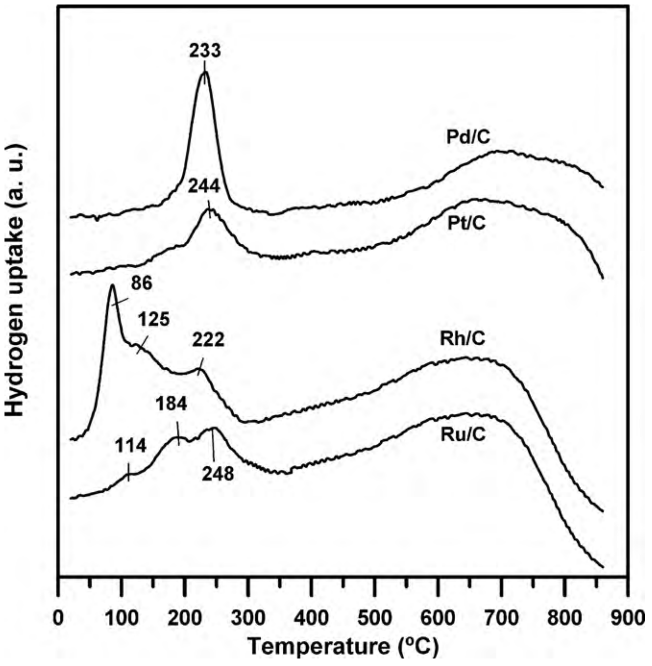

Fig. 1. TPR profiles of the fresh catalysts.

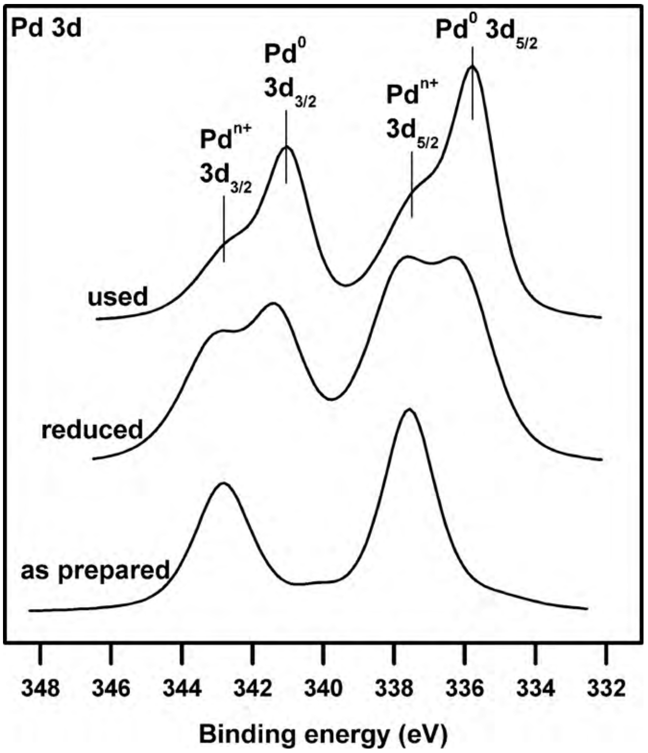

Fig. 2. Pd 3d core level XPS spectra of Pd/C catalyst: (a) fresh unreduced; (b) after reduction in H_2 at 250 °C; and (c) after used in HDC of DCM.

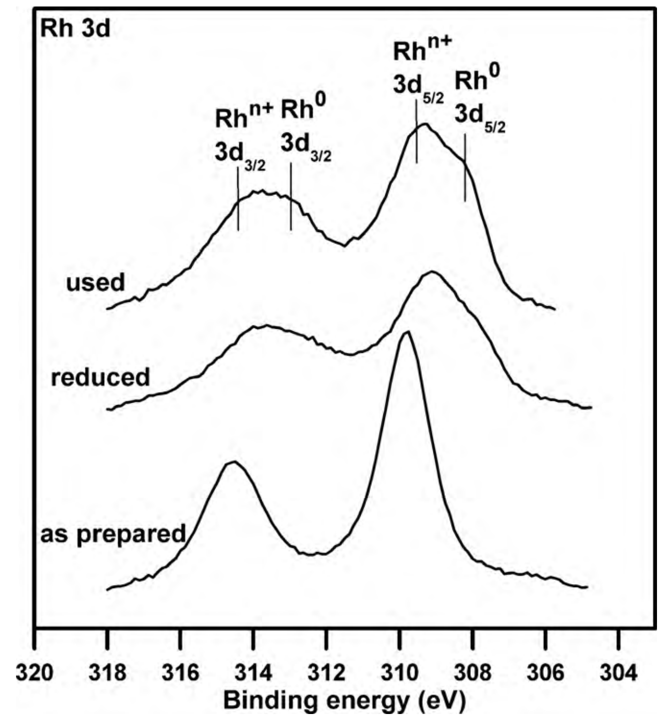

Fig. 3. Rh 3d core level XPS spectra of Rh/C catalyst: (a) fresh unreduced; (b) after reduction in H_2 at 250 °C; and (c) after used in HDC of DCM.

interaction of Ru with the carbon surface. In other works, dealing with $Pd/CeO_2–Sm_2O_3$ catalysts [48,49] two peaks were found for the reduction of Pd related to different locations of Pd particles evidenced by XPS and TEM. Nevertheless, further research is needed for a more conclusive knowledge on this point. All the samples were reduced at 250 °C in the transient conditions of the TPR experiments, which assures the reduction of the catalysts precursors at this temperature under the conditions used in the activity tests.

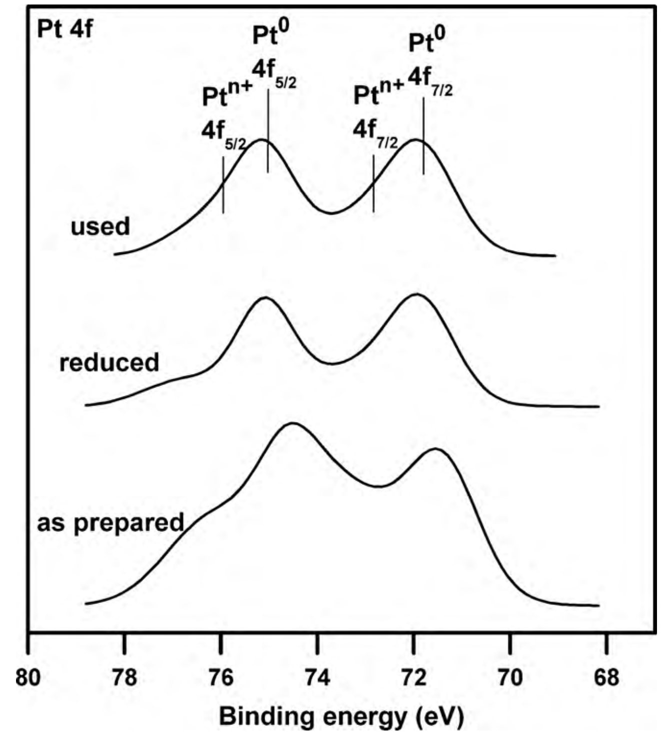

Fig. 4. Pt 4f core level XPS spectra of Pt/C catalyst: (a) fresh unreduced; (b) after reduction in H_2 at 250 °C; and (c) after used in HDC of DCM.

Table 1
Metal content, BET surface area and metal dispersion of the fresh and used (65 h time-on-stream) catalysts.

Catalyst	Metal content (%)	S_{BET} (m^2/g)	Pore volume (cm^3/g)	D (%)
Pd/C	0.84	1236	0.52	38
Pt/C	0.85	1191	0.52	40
Rh/C	0.78	1200	0.54	49
Ru/C	0.83	1160	0.52	62
Pd/C used	0.85	1282	0.57	9
Pt/C used	0.83	1201	0.53	95
Rh/C used	0.80	1209	0.58	27
Ru/C used	0.81	1082	0.49	15

Table 1 summarizes the values of BET surface area, pore volume, bulk metal content and metal dispersion of the catalysts fresh and after 65 h time on stream. In all cases, the metal content determined by ICP-MS was lower than the nominal 1% load used for impregnation.

The 77 K N_2 adsorption–desorption isotherms of the catalysts approached in all cases to Type 1 of the BDDT classification, being indicative of microporous solids, although a contribution of mesopores is also present in some extent. All of them show a high BET surface area, with values well above 1000 m^2/g, even for the used catalysts, indicating that no significant constriction or partial blockage of the porous structure occurs upon reaction at the relatively mild temperatures used in the experiments.

Results of CO and H_2 chemisorption showed that all the fresh catalysts were fairly well dispersed. Metal dispersion of Pd/C and Pt/C was very similar, with values between 38 and 40%. For Rh/C and Ru/C higher dispersions were observed, especially for the Ru catalyst that presents the highest value (62.3%). A significant decrease of dispersion was observed upon use in DCM hydrodechlorination except for the Pt/C catalyst whose dispersion increased up to about 95%. The increase of dispersion has been observed by other authors, although less pronounced, for Pd and Pt on activated carbon catalysts in the hydrodechlorination of other organochlorinated compounds [20,25]. They ascribed the re-dispersion of metallic particles to the presence of HCl that involves the formation, volatilisation and re-deposition of unstable metallic halides. These halides can be reduced by the high concentration of H_2 introduced as reactant. Ordonez et al. [20] observed re-dispersion of Pd and Pt in the hydrodechlorination of tetrachloroetilene with commercial catalysts, while in Mori et al. studies of hydrodechlorination of CFC-113 with Pd, Pt, Rh and Ru [25], re-dispersion was only found with Pt.

Figs. 2–4 show the XPS profiles of as prepared and reduced fresh Pd/C, Rh/C and Pt/C catalysts, as well as after being used. In the case of Ru, no suitable profiles were found where the peaks could be deconvoluted. The low intensity of the spectra indicated that the concentration of Ru in the outer surface of the catalyst particles was very low, thus suggesting that Ru is preferentially deposited inside the internal pores. This is consistent with the TPR results, where most of Ru was reduced at a high temperature, denoting a strong interaction with the support. According to the XPS profiles (Figs. 2–4), the metals are in two different oxidation states, which can be attributed to zero-valent and electro-deficient species. The formation of electro-deficient species in metallic catalysts is well established in the literature [50–54]. It is well known that formation of electro-deficient species highly depends on the nature of the support, as well as on the metal precursor and the preparation method. The formation of electro-deficient species in Pd/C catalysts prepared from H_2PdCl_4 has been widely investigated in previous

Table 2
Chlorides content of the catalysts measured by XPS.

Catalyst	% Cl_{2p}	Inorganic (B.E. 198–199 eV)	Organic (B.E. 200–202 eV)
Pd/C as prepared	0.57	49.2	50.8
Pd/C reduced	0.11	46.8	53.2
Pd/C used	0.13	29.2	70.8
Pt/C as prepared	0.43	37.6	62.4
Pt/C reduced	0.13	17.0	83.0
Pt/C used	0.14	18.5	81.5
Rh/C as prepared	0.85	57.7	42.3
Rh/C reduced	0.38	54.9	45.1
Rh/C used	0.51	48.5	51.5
Ru/C as prepared	0.74	39.0	61.0
Ru/C reduced	0.23	18.7	81.3
Ru/C used	0.23	7.2	92.8

works [1,18,30]. A main band centered at a binding energy of 337 eV was observed for Pd $3d_{5/2}$ in the as prepared unreduced catalyst. Two main bands centered at binding energy values around 335.5 and 337 eV were observed for Pd $3d_{5/2}$ in the reduced catalyst, which can be attributed to metallic palladium (Pd^0) and electro-deficient palladium (Pd^{n+}), respectively. Integration of the areas under the curves yields fairly similar relative proportions of these two species as it was found in previous studies [1,18,30]. In the case of Rh/C, in the as prepared catalyst a main band appears at a binding energy of 307.5 eV while two bands were observed around 307.5 and 309.8 eV for Rh $3d_{5/2}$ in the reduced and used catalysts, which can be attributed to metallic (Rh^0) and electro-deficient (Rh^{n+}) rhodium. The use of the Pd and Rh catalysts in the HDC reaction leads to a decrease of the relative amount of the electro-deficient species. However, the Pt catalyst shows much higher proportion of metallic species than the other catalysts. The band at a binding energy of 72 eV for Pt $4f_{7/2}$ corresponds to Pt^0 while the value around 73.4 eV corresponds to Pt^{n+}. No significant differences were found in this case between the fresh reduced and the used catalyst. Table 2 shows inorganic and organic chlorides contents of the catalysts obtained from the deconvolution of the Cl_{2p} XPS spectra. As expected, the chlorides content highly decreased after reduction of the catalysts. When fresh reduced and used catalysts are compared, a significant increase in the proportion of organic chlorides is observed after the use in the HDC reaction of Pd/C, Rh/C and Ru/C catalysts, which can be attributed to the poisoning of the active centers with organochlorinated compounds.

Fig. 5 shows the XRD profiles of the fresh catalysts reduced and after being used in the HDC of DCM. Peaks corresponding to metallic particles are not observed for the fresh Pt, Rh and Ru catalysts, suggesting a high metal dispersion. However, in the XRD pattern of fresh Pd/C a small peak at $2\theta = 40^\circ$ was found, corresponding to the (1 1 1) planes of metallic Pd in the cubic system. This can be attributed to a wide distribution of Pd particles size, since a fairly good dispersion value was obtained by chemisorption. A similar intensity of the peak was found in the used catalyst, which suggests that no metal sintering takes place under reaction conditions. Nevertheless, this peak is displaced to a lower scattering angle ($2\theta = 39^\circ$) respect to that of the fresh catalyst. This can be due to Pd hydrides, although some authors [20,55] attribute this shift to the formation of a Pd–C solid solution after the use of Pd/C catalysts in similar reactions. The absence of diffraction peaks in the patterns of used Pt/C and Rh/C catalysts indicates that no sintering of metallic particles occurred during the reaction. On the contrary, in the case of Ru/C a peak appears at $2\theta = 40^\circ$ for the used catalyst, indicating that metal sintering took place during the reaction. The decrease in the dispersion for Pd and Rh catalysts can be ascribe to the poisoning of active centers with reactants, intermediates and/or reaction products as it will be further explained within the text.

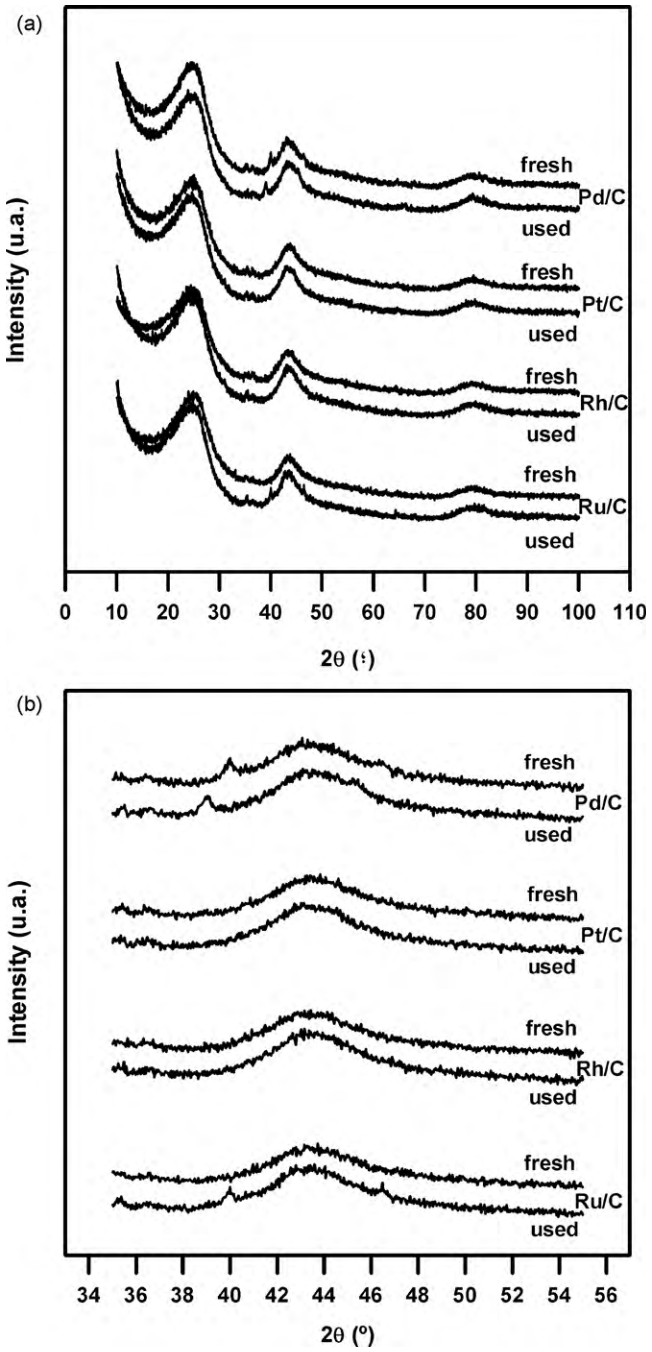

Fig. 5. XRD patterns of the fresh and used catalysts: (a) normal scale, $2\theta = 1–110^\circ$; (b) expanded, $2\theta = 34–56^\circ$.

3.2. Catalytic activity

Figs. 6–9 show the conversion and selectivity results obtained at different reaction temperatures with the four catalysts tested, at two space-time values. All of the catalysts show fairly active with DCM conversion values between 89 and 99% at the highest space-time and temperature investigated. As can be seen, DCM conversion significantly increases with temperature in the range explored (200–250 °C). Rh/C shows the highest activity (Fig. 8) and Pt/C the lowest (Fig. 7). All the catalysts were very selective to non-chlorinated compounds but some significant differences were found in the selectivity patterns. The selectivity to monochloromethane decreased somewhat when increasing the reaction temperature in the cases of Pd, Pt and Rh while the oppo-

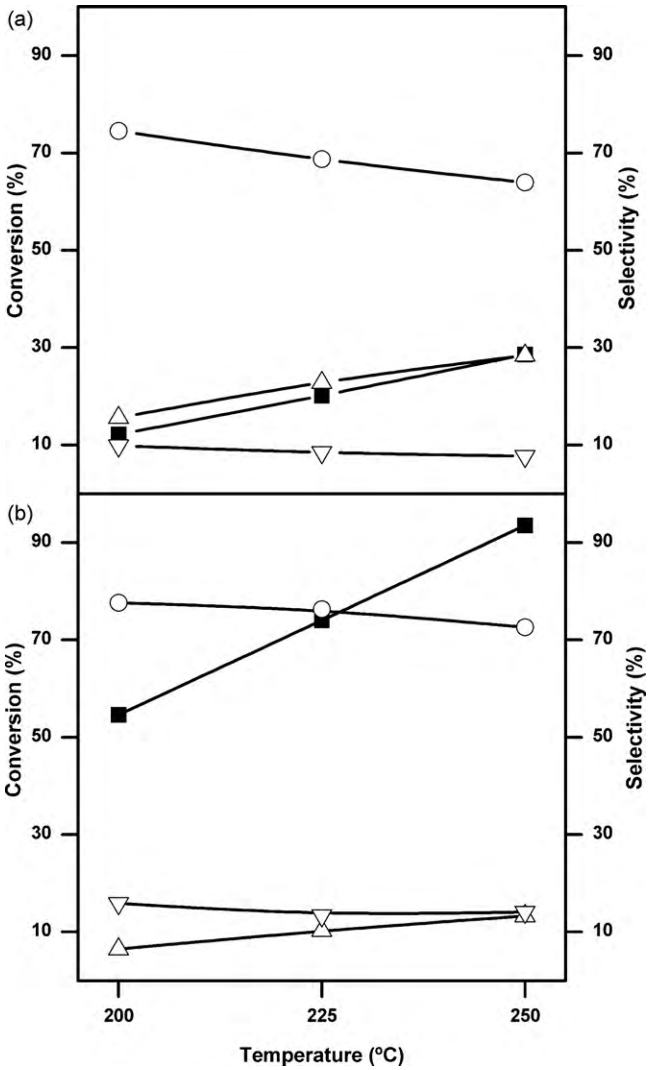

Fig. 6. Effect of temperature on the activity and selectivity to reaction products in the HDC of DCM with Pd/C catalyst at 0.08 (a) and 1.73 kg h mol^{-1} (b) space-time. (■) Conversion; (○) methane; (△) ethane; and (▽) monochloromethane.

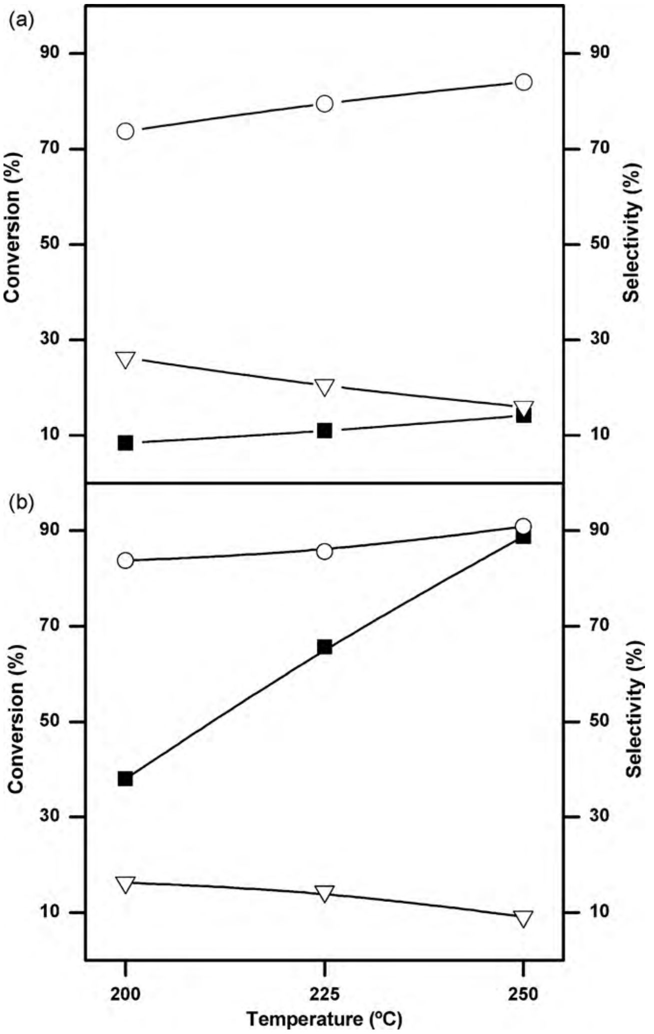

Fig. 7. Effect of temperature on the activity and selectivity to reaction products in the HDC of DCM with Pt/C catalyst at 0.08 (a) and 1.73 kg h mol^{-1} (b) space-time. (■) Conversion; (○) methane; and (▽) monochloromethane.

site was found for Ru. Regarding to products distribution, the main differences are observed with the Pt/C catalyst. Methane is the main reaction product in all cases, but hydrodechlorination of dichloromethane with Pt/C catalyst exclusively yields methane and monochloromethane (traces of ethane and propane were detected at 250 °C), while hydrocarbons higher than CH_4 were also obtained with the rest of the catalysts. The use of Pd/C leads to the formation of ethane and a wider diversity of reaction products were obtained with Rh and Ru including significant amounts of propane and even butane. The formation of hydrocarbons higher than CH_4 seems to be related with the electro-deficient metal species. The Pt/C catalyst, which yielded only methane, shows a very small amount of electro-deficient Pt once reduced (Fig. 4) whereas Pd/C and Rh/C that presented significant amounts of electro-deficient species (Figs. 2 and 3), led to the formation of hydrocarbons of more than one carbon atom. In previous studies dealing with the hydrodechlorination of carbon tetrachloride and DCM with Pd/C catalysts [1,18,30] the existence of a dual active center constituted by the association of neighbouring metallic and electron-deficient palladium species: [$Pd^0 + Pd^{n+}$] was found. Hydrogen chemisorbs and homolytically dissociates on Pd^0, whereas the chloromethane is chemisorbed on a single Pd^{n+} site. Though the action mechanism of Pt/C catalyst may be different, the formation of higher hydrocarbons seems to require the reaction of two organochloride radicals adsorbed on neighboring electro-deficient metal sites. Thus, a lower concentration of these sites in the catalyst would reduce the formation of those compounds. In the cases where higher hydrocarbons are formed, the reaction temperature has a significant influence on the products distribution, the selectivity to those species being favoured, in detriment of methane by increasing the temperature (Figs. 6, 8 and 9). The Ru/C catalyst showed the highest selectivity to hydrocarbons higher than CH_4. The similarity with Pd/C and Rh/C in the selectivity patterns suggests the existence of electro-deficient species also in that catalyst.

The higher metal dispersion of Ru/C catalyst can be related with a different location of the metal particles. As stated before, Pd/C, Rh/C and Pt/C showed a significant amount of metal particles in the outer surface of the catalysts, since fairly good XPS spectra were obtained (Figs. 2–4) whereas the low intensity of the 3p spectra of the Ru/C catalyst suggests that Ru particles are mainly located in the internal pores.

3.3. Stability tests

The evolution of DCM conversion and selectivity to reaction products with time-on-stream is depicted in Figs. 10–13 at 1.73 kg h mol^{-1} space-time and 250 °C. The activity of the catalysts

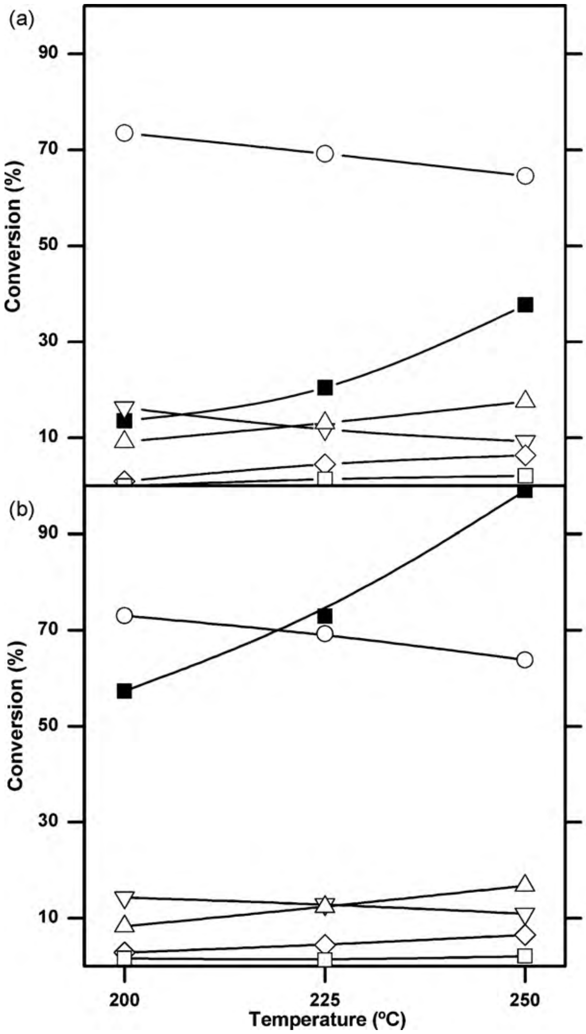

Fig. 8. Effect of temperature on the activity and selectivity to reaction products in the HDC of DCM with Rh/C catalyst at 0.08 (a) and 1.73 kg h mol^{-1}; (b) space-time. (■) Conversion; (○) methane; (△) ethane; (◊) propane; (▽) monochloromethane; and (□) butane.

varies upon time-on-stream in a different way. The Pt/C catalyst showed highly stable along the 65 h of the test (Fig. 11). Catalysts with such stability have not been reported previously for the hydrodechlorination of DCM. Mori et al. [25] observed an increase of conversion upon time-on-stream in the hydrodechlorination of CFC-113 with a Pt catalyst which explained by an increased dispersion of Pt particles. In our case, the conversion of DCM remained constant although the dispersion of Pt increased upon time-on-stream (Table 1). As can be seen in Fig. 11, the selectivities to methane and monochloromethane remained also constant.

Partial deactivation was observed for the rest of the catalysts in different extents. The loss of activity was more pronounced in the case of Ru and Pd showing Rh significantly less deactivation. The conversion over Ru/C decreased from 94 to 50% after 20 h of operation that of PdC decreased from 93 to 55% after 65 h while for Rh the decrease was only from 99 to 90% after the same time-on-stream. As indicated before, no significant constriction of the porous structure seems to occur under the operating conditions of the experiments (Table 1), so that deactivation cannot be attributed to any textural modification. A clear relationship can be established between the decrease in the amount of exposed metal upon reaction, measured by chemisorption (Table 1), and the loss of activity. Ru/C and Pd/C catalyst showed the most marked deactivation and also the high-

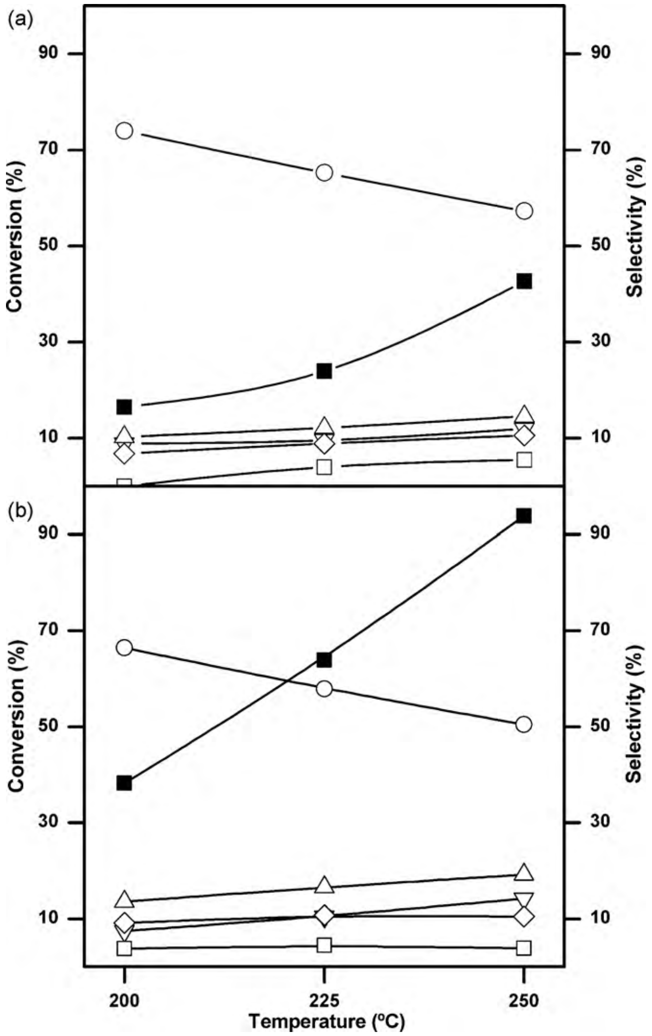

Fig. 9. Effect of temperature on the activity and selectivity to reaction products in the HDC of DCM with Ru/C catalyst at 0.08 (a) and 1.73 kg h mol^{-1} (b) space-time. (■) Conversion; (○) methane; (△) ethane; (◊) propane; (▽) monochloromethane; and (□) butane.

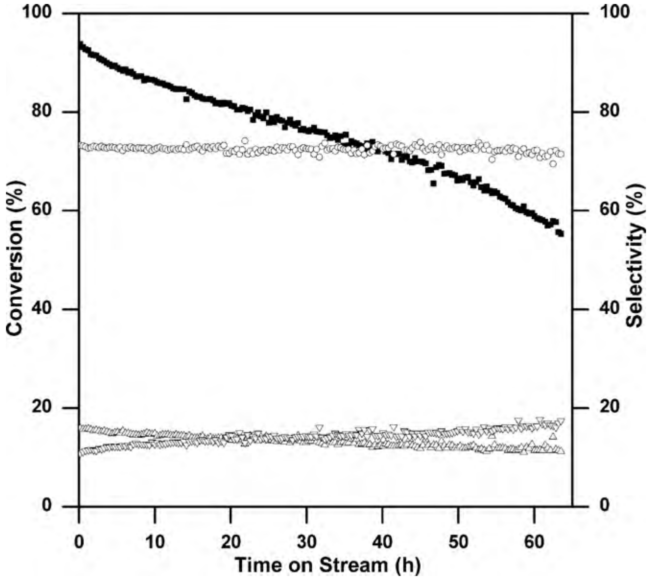

Fig. 10. Evolution of dichloromethane conversion and selectivity to reaction products upon time-on-stream with Pd/C at 250 °C and 1.73 kg h mol^{-1} space-time: (■) Conversion; (○) methane; (△) ethane; and (▽) monochloromethane.

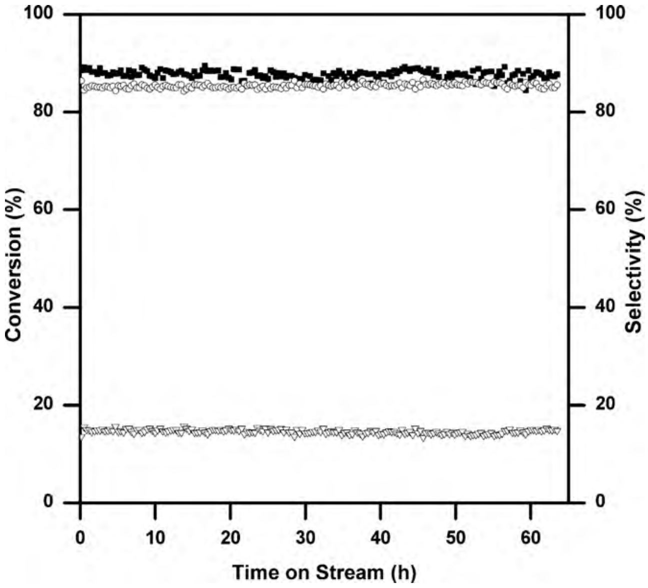

Fig. 11. Evolution of dichloromethane conversion and selectivity to reaction products upon time-on-stream with Pt/C at 250 °C and 1.73 kg h mol^{-1} space-time: (■) Conversion; (○) methane; and (▽) monochloromethane.

est decay of dispersion. The highly stable Pt/C catalyst, not only did not show any decrease of metal dispersion upon reaction but even a significant improvement was observed. Growing of metal particle size was observed in the Ru/C catalyst by means of XRD (Fig. 5), so that, metal sintering of Ru particles seems to be one of the causes of deactivation of this catalyst. However, in the case of Pd/C and Rh/C sintering of metal particles could not be proved by XRD (Fig. 5). The decrease in the Pd and Rh dispersion can be attributed to the poisoning of the active centers with reactants, intermediates and/or reaction products, since no sintering appears to occur.

The important decrease in metal dispersion and subsequent deactivation of Pd/C and Rh/C catalysts can be related with a decrease in the proportion of the electro-deficient species as shown by the XPS spectra (Figs. 2 and 4). This decrease was more pronounced for the Pd catalyst. Assuming that dissociative adsorption of dichloromethane takes place mainly on that metal species, deactivation can be attributed in a great part to the poisoning of the active centers with reactant, intermediates and/or reaction products, which cause a reduction of the accessible metal surface. In fact, an increase in the amount of organic chlorides was observed in the used catalysts by means of XPS (Table 2). The higher poisoning of Pd centers can be explained by a stronger interaction with organochloride radicals due to the higher local density of non-occupied states at the Fermi level N(Ef) compared with other metals, like Rh, as a consequence of its particular electronic structure [43,56–58]. Coke deposition does not appear to be a cause of deactivation since in that case it would be expected a reduction in the BET surface area, and a greater deactivation in the hydrodechlorination of DCM over Rh/C as it leads to much higher amounts of hydrocarbons. Nevertheless, further evidences would be needed to confirm this conclusion.

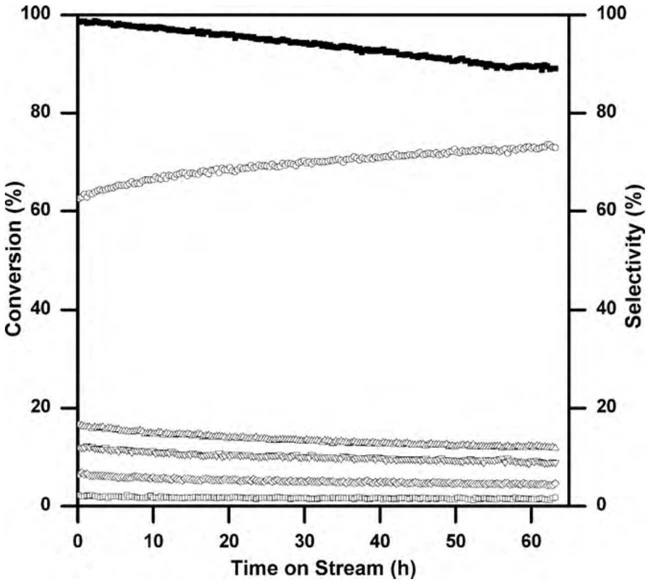

Fig. 12. Evolution of dichloromethane conversion and selectivity to reaction products upon time-on-stream with Rh/C at 250 °C and 1.73 kg h mol^{-1} space-time: (■) Conversion; (○) methane; (△) ethane; (◊) propane; (▽) monochloromethane; and (□) butane.

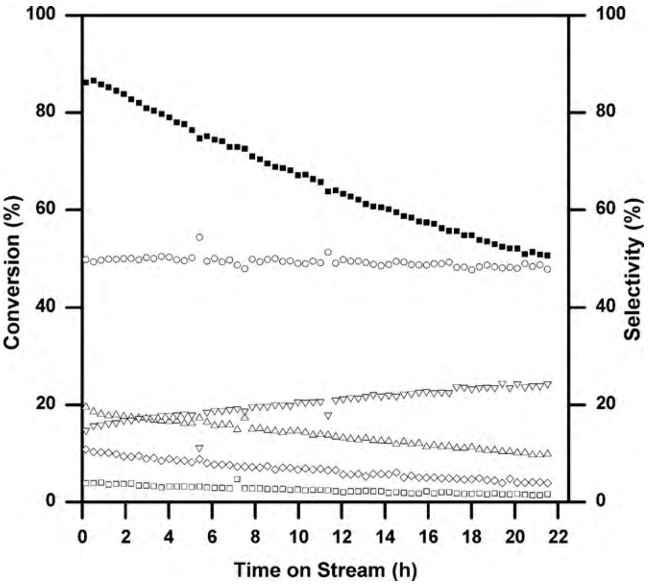

Fig. 13. Evolution of dichloromethane conversion and selectivity to reaction products upon time-on-stream with Ru/C at 250 °C and 1.73 kg h mol^{-1} space-time: (■) Conversion; (○) methane; (△) ethane; (◊) propane; (▽) monochloromethane; and (□) butane.

In contrast with Pd/C and Rh/C catalysts, Pt/C, which did not suffer any deactivation upon the 65 h time-on-stream of the experiment, had a very low proportion of electro-deficient species which did not change significantly upon reaction (Fig. 4). The fast deactivation of the Ru/C catalyst could be explained by the contribution of two phenomena, sintering of metal particles and poisoning by reactant, intermediates and/or reaction products.

In general the selectivity did not show significant changes upon time-on-stream. In the cases of Pd/C and Ru/C the selectivity to monochloromethane slightly increased in detriment of hydrocarbons higher than CH_4, while methane selectivity remained almost constant. In the case of Rh/C, the selectivity to methane slightly increased along the operation time.

4. Conclusions

The activated carbon-supported catalysts prepared using Pd, Pt, Rh and Ru as active phases showed effective for HDC of DCM. High selectivities to non-chlorinated compounds were found, higher than 80% in all cases. Nevertheless, significant differences were found in the stability patterns. The Pt catalyst showed the highest resistance to deactivation under the working conditions used, the activity remaining constant upon the 65 h time-on-stream of the stability tests performed. A significant loss of activity upon time-on-stream was observed for the Pd and Ru catalysts, more pronounced for the latter, while the Rh catalyst showed a better behavior. Deactivation can be related with a decrease of the exposed metal surface. In the cases of Pd and Rh, this reduction can be attributed to the poisoning of active centers with chlorinated reactants intermediates and/or reaction products. The loss of activity observed for Ru/C seems to be mainly due to metal sintering during the reaction, though contribution of poisoning cannot be rejected. The Pt catalyst gave a simple product distribution yielding only methane and monochloromethane as reaction products. Ethane was also found in the case of Pd/C whereas a wider diversity of reaction products was obtained with Rh/C and Ru/C where the formation of hydrocarbons up to four carbon atoms was observed. Methane was the main reaction product in all the cases. The selectivity patterns did not change significantly upon time-on-stream.

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