Repositorio Institucional de la Universidad Autónoma de Madrid

<https://repositorio.uam.es>

Esta es la **versión de autor** del artículo publicado en:

This is an **author produced version** of a paper published in:

Industrial & Engineering Chemistry Research 58.45 (2019): 20592-20600

DOI: <https://doi.org/10.1021/acs.iecr.9b04262>

Copyright: © 2019 American Chemical Society

El acceso a la versión del editor puede requerir la suscripción del recurso

Access to the published version may require subscription

Selectivity to olefins in the hydrodechlorination of chloroform with activated carbon-supported palladium catalysts

C. Fernandez-Ruiz¹, J. Bedia¹, S. Andreoli², S. Eser², J.J. Rodriguez¹,
L.M. Gómez-Sainero^{1,*}

1 Department of Chemical Engineering, Facultad de Ciencias, Universidad Autónoma de Madrid, Campus de Cantoblanco, E-28049, Madrid, Spain.

2 EMS Energy Institute and Department of Energy and Mineral Engineering, Penn State University, 114^a Hosler Building, University Park, PA 16802, USA.

**Corresponding author details: Telephone number: 34 91 497 6939
E-mail: luisa.gomez@uam.es.*

Abstract

This study analyzes the selectivity of Pd (1 wt%) catalysts supported on different activated carbons to produce olefins from hydrodechlorination of chloroform. It was found that selectivity to olefins was favoured by a higher zero-valent to electrodeficient Pd ratio ($\text{Pd}^0/\text{Pd}^{n+}$) and by a lower amount of oxygen-containing surface functional groups on the activated carbon supports. Thus, the highest selectivity to olefins was obtained by catalysts supported on FeCl_3 and ZnCl_2 --activated carbons. Conversely, the catalysts supported on KOH-, NaOH-, and H_3PO_4 -activated carbons gave the lowest selectivity to olefins. These catalysts showed higher surface concentrations of electro-deficient Pd as well as high concentrations of oxygen functional groups that enhance the adsorption of reactants and intermediates. This leads to complete hydrogenation of reaction intermediates and poisoning of active sites by the adsorption of chlorocarbon compounds. ZnCl_2 -derived catalysts with the highest selectivity to olefins also showed an outstanding

stability, most likely due to re-dispersion into very small and well-distributed Pd particles during the reaction. However, FeCl_3 -derived catalysts gave rise to sintering of Pd particles, resulting in a marked loss of activity.

Keywords: Selectivity; olefins; hydrodechlorination; chloroform; activated carbon; palladium.

Introduction

Chloromethanes are toxic and harmful species^{1,2} emitted in gas streams from different industrial processes, and therefore, their release to the atmosphere is submitted to stringent regulations. There are several techniques available for the removal of these compounds. However, their transformation into valuable hydrocarbons, such as low molecular weight olefins, ethylene and propylene, has much more interest. These are well-known key petrochemicals^{3,4} that are currently produced in energy-intensive industrial processes⁵. In addition, chloromethanes can be used as intermediates in the conversion of methane to olefins.

The valorization of methane by activation using halogen intermediated processes at mild conditions followed by a dehalogenation pathway, for the production of olefins, is attracting much interest in the recent literature⁶. The halogen intermediated processes have been successfully used in other industrial processes such as the production of polymer and fine chemicals⁷. The reactivity of the radicals taking part in the halogenation of methane depends on the halogen, chlorine and bromine being the most thermodynamically favorable^{8,9}. Bromination shows a better selectivity control, but chlorination has the advantages of being a well established industrial process and chlorine is more readily available and cheaper than bromine.

Catalytic hydrodechlorination (HDC) can be considered as a good alternative for the valorization of chloromethanes into olefins. It operates under moderate conditions of temperature and pressure and has been widely studied for the treatment of chloromethanes with the objective of converting these pollutants into species with lower toxicity. However, the transformation of chloromethanes into olefins remains still as a challenge

¹⁰. Some authors ^{11,12} found the formation of C2-C4 hydrocarbons in the HDC of carbon tetrachloride with Pd/C catalysts. However, in these studies, the amount of olefins was not reported, the selectivity to methane was very high (> 40% in most of the cases) and the catalyst were deactivated in less than ten hours. The HDC of a mixture of different chloromethanes to obtain high-valued olefins was also investigated ¹⁰. The results were promising in terms of conversion and selectivity, but no long-time on-stream stability was reported. Other studies presented good results on the dechlorination of monochloromethane to olefins using molecular sieves like ZSM-5, HZSM-5, SAPO-34 and HSAPO-34 as catalysts ^{13–17}, but they suffered a rapid deactivation, which is a limiting factor for the application of this technology. The catalysts most commonly used in gas-phase HDC are composed of a metallic active phase (such as, Pt, Pd, and Rh) supported on different porous materials, such as activated carbons ¹⁸, zeolites or zirconia ^{19–23}, among others. We recently studied ²⁴ the behaviour of Pd, Pt, Rh and Ru catalysts in the hydrodechlorination of chloromethanes to yield ethane and ethylene. It was confirmed, by both computational and experimental approaches, that Pd was the most suitable active phase for the valorisation of chloromethanes into C2 hydrocarbon. In a subsequent work, we studied the chloroform conversion into ethane and propane by catalytic HDC with Pd supported on activated carbons obtained from lignin by chemical activation with different agents ²⁵. The highest selectivities to ethane and propane were obtained with the catalysts supported on KOH- and NaOH-activated carbons, which showed the highest surface areas and the lowest Pd⁰/ Pdⁿ⁺ ratios. Nevertheless, the selectivity to olefins was almost negligible and, therefore, the performance of the catalysts needs to be optimized. Other studies have reported higher selectivities to olefins using supported Pd catalysts in the HDC of 1,2-dichloroethane ^{21,23,26,27} instead of more common chloromethanes, such as chloroform (TCM) or dichloromethane (DCM).

The aim of this study was to formulate a stable catalyst to obtain high yields of olefins (ethylene and/or propylene) from the hydrodechlorination of trichloromethane (TCM) that is used as a model chloromethane. In addition, a principal focus was placed on understanding the key factors that affect the selectivity to olefins in hydrodechlorination reactions. Based on a previous work²⁵, Pd catalysts were prepared that are supported on activated carbons of tuneable properties obtained by chemical activation of lignin. Special attention was given to understanding how changes in carbon surface chemistry and reaction conditions (H_2 :TCM molar ratio, reaction temperature and space time) affect the selectivity to producing olefins. The stability of the catalysts and the modifications that catalysts undergo during the reaction were also monitored in detail. The analysis of the physico-chemical properties of the catalysts and their performance in the hydrodechlorination reactions allowed establishing structure-performance relationships that are useful for designing catalysts that are highly selective to olefins and stable during hydrodechlorination reactions.

Experimental Section

Granit lignin was obtained from Granit S.A. (Switzerland, C: 61.6%; H: 6.0%; N: 1.1%; S: 0.2%; ash content = 2.0 w.t. %). $ZnCl_2$ (>99%), KOH pellets (>85%), H_3PO_4 (85%), $PdCl_2$ (99%) and HCl (37%) were supplied by Panreac; anhydrous $FeCl_3$ (>98%) from Riedel-de Haën and NaOH pellets (95%) from Scharlau. Chloroform (0.4 % mol in N_2), H_2 and N_2 (both 99.999 % purity) were provided by Praxair.

Five activated carbons were synthesized as supports by chemical activation of lignin with FeCl_3 , ZnCl_2 , H_3PO_4 , KOH and NaOH . The activation procedures were described elsewhere ²⁵. Briefly, lignin was physically mixed with each activating agent at a mass ratio (activating agent:lignin) of 3:1 with ZnCl_2 , FeCl_3 and H_3PO_4 , and 4:1 with NaOH and KOH . The impregnated samples were heated for two hours at the activating temperature, under nitrogen atmosphere, in a tube furnace electrically heated. The activation temperature was 500 °C in the case of ZnCl_2 and H_3PO_4 , and 800 °C for NaOH , KOH and FeCl_3 , always reached at 10 °C·min⁻¹ heating rate. After cooling to room temperature under the nitrogen atmosphere, the resulting samples were washed with HCl aqueous solution 0.1 M at 70 °C, under continuous stirring (300 rpm) for 3 hours and using a ratio of 200 cm³ of the HCl aqueous solution per gram of recovered sample. Later, washing was carried out with distilled water until neutral pH of the eluate, followed by drying at 60 °C for 24 h. The activated carbons were denoted by the representative element of the activating agent (Fe, P, Na, K and Zn) followed by C.

The active metal phase was in all cases Pd, deposited by incipient wetness impregnation, with a 1 M HCl aqueous solution of PdCl_2 , for a nominal 1 % of Pd in weight. After impregnation, the samples were dried for 12 hours at 70 °C in an oven. The catalysts were named by the notation of the support, followed by Pd (for instance, ZnCPd).

The porous texture of the catalysts was characterized by N_2 adsorption-desorption at -196 °C on a Tristar II 3020 apparatus (Micromeritics). Previously, all the samples were outgassed for 12 hours at 150 °C in a VacPrep 061 (Micromeritics). The BET equation was used to calculate the specific surface area (A_{BET}), while external surface area (A_{EXT}) was calculated using t-method. X-ray diffraction (XRD) spectra of the catalysts were

obtained in a PANalytical XPert PRO diffractometer. The samples were scanned using CuK α monochromatic radiation ($\lambda = 1.5406 \text{ \AA}$, 45 kV, 40 mA) with an X'Celerator detector. The scan range was 4-90° (2 θ) with a collection time of 20 seconds. The external surface composition was analysed by X-ray photoelectron spectroscopy (XPS) with a Thermo Scientific apparatus with Al K α radiation (1486.7 eV). General spectra were recorded for the samples by scanning binding energy (BE) from 0 to 1200 eV. Corrections for changes in BE caused by sample charging were corrected by taking the C 1s peak (284.5 eV) as an internal standard. The size distribution of Pd particles and morphologies of the five catalysts were analysed by transmission electron microscopy (TEM). TEM images were obtained using a JEM 2100 microscope from JEOL Company with an accelerating voltage of 200 kV, with a resolution between points of 0.25 nm. Particle size distributions were obtained from more than 100 particles. Chemical and size distribution analysis of the metallic particles of FeCPd and ZnCPd used in the HDC reaction were further performed with a FEI Tecnai F30 microscope, operated at STEM mode and 300 kV, with a high-angle annular darkfield detector (HAADF) and equipped with an EDS detector (EDAX). Those catalysts samples were selected because of their higher selectivity to olefins but opposite deactivation behaviour. Both samples were previously dispersed in ethanol and dropped onto holey carbon-coated Cu grids.

Mass spectrometry coupled to temperature programmed desorption (MS-TPD) experiments were carried out on a Micromeritics TPD/TPR 2910 equipment, using 120 mg of sample powder placed in a quartz tube. After 30 minutes 120 °C in Ar flow, the samples were heated at 10 °C/min to 900 °C and maintained at that temperature for 15 minutes. The exit gas stream was analyzed by an on-line quadrupole mass spectrometer

(Ametek Dycor, USA) to determine the amounts of CO₂ and CO evolved. The fitting of the TPD peaks was performed by least squares using Gauss peak shapes.

The HDC experiments were performed at atmospheric pressure in a continuous flow reaction system (Micro-Activity, from PID) described elsewhere²⁴, consisting of a quartz tube (3 mm internal diameter) where the catalyst was placed. The reactor exit was coupled to a gas chromatograph (Varian, CP-SilicaPLOT 60m) with a FID detector. The catalysts were previously reduced “in situ” under H₂ atmosphere (50 Ncm³ min⁻¹) at the selected temperature for 2 hours. The HDC runs were carried out with 100 cm³·min⁻¹ of total flow rate (N₂+TCM+H₂), a TCM inlet concentration of 1000 ppmv (resulting in a space time $\tau = 0.2 \text{ kg h mol}^{-1}$) and different H₂:TCM molar ratios (100/50/25/10:1). The reaction temperature was raised from 75 up to 350 °C, and the long-term, steady state experiments were performed at 300 °C..

The performance of the catalysts was evaluated in terms of TCM conversion (X), selectivity to the different reaction products (S_i) and yield (Y_i), calculated by:

$$X (\%) = \frac{\text{TCM}_{\text{inlet}} - \text{TCM}_{\text{outlet}}}{\text{TCM}_{\text{inlet}}} \cdot 100$$

$$S_i (\%) = \frac{n_i^{\text{outlet}} \cdot N_{C,i}}{n_i^{\text{outlet}} \cdot N_{C,i} + n_j^{\text{outlet}} \cdot N_{C,j} + \dots} \cdot 100$$

$$Y_i (\%) = \frac{n_i^{\text{outlet}} \cdot N_{C,i}}{n_{\text{TCM}}^{\text{inlet}}} \cdot 100$$

where n_i^{outlet} and n_i^{inlet} are the ppmv of the product i at the reactor outlet and inlet, $N_{C,j}$ and

$N_{C,i}$ are the number of carbon atoms in the compound j and i respectively.

Results and Discussion

The effect of reduction temperature on the catalytic activity was evaluated with KCPd catalyst, which showed the best selectivity to hydrocarbons other than methane (C_{1+}) in a previous work ²⁵. The evolution of TCM conversion with reaction temperature using that catalyst previously reduced at 250, 300 and 350 °C is given in Figure S1 of supporting information. No significant differences were found. However, regarding the selectivity to olefins (Figure S2), the catalyst reduced at 300 °C gave the highest values at the different reaction temperatures used. Therefore, this reduction temperature was selected for the rest of the study. HDC of TCM led to methane, ethane, propane, ethylene and propylene, accompanied by traces of butane and butene. Monochloromethane (MCM) and dichloromethane (DCM) were also detected as incomplete dechlorination by-products. It is worth mentioning that with this reduction temperature the selectivity to chloromethanes (MCM and DCM) was always below 5% and the carbon balance was closed at >95%.

The H_2 /TCM molar ratio can have a significant effect on the selectivity of the reaction. Decreasing this molar ratio usually increases the selectivity to olefins, though it also reduces the rate of TCM conversion and can negatively affect the stability of the catalyst. The results of TCM conversion versus reaction temperature with the KCPd catalyst at four different H_2 /TCM molar ratios are given in Figure S3. Conversion significantly increased up to H_2 /TCM molar ratio of 50, and beyond that value, no significant effect was observed. Figure 1 depicts the effect of H_2 /TCM molar ratio on the yield to olefins at different reaction temperatures with the KCPd catalyst. In general, the yield increases up to H_2 /TCM molar ratios in the range 25-50 and then decreases beyond that value. The high selectivities achieved at a H_2 /TCM molar ratio of 50 are accompanied by a deeper dechlorination and, therefore, this molar ratio was selected for the rest of the experiments.

The effect of the reaction temperature on TCM conversion is given in Figure 2. As expected, in general, the conversion increases with the reaction temperature, except for a slight decrease at the highest temperatures tested (300 °C) with NaCPd and FeCPd, attributed to the significant deactivation suffered by these catalysts at that temperature. In contrast, a complete conversion of TCM was achieved at 250-300 °C with the three other catalysts. Figure 3 shows the selectivity to olefins and paraffins at different reaction temperatures with the catalysts that are more selective to olefins (KCPd, FeCPd and ZnCPd). In the three cases, the selectivity to olefins increased with temperature, except for ZnCPd within the 125-200 °C range, of minor relevance. At low reaction temperatures, methane and ethane were the main reaction products, followed by propane. As the reaction temperature increased, the selectivity to these products decreased significantly in favour of ethylene and propylene, especially with the FeCPd and ZnCPd catalysts. A reaction temperature of 300 °C was selected to check the stability of the catalysts in long-term experiments and compare the performance of all the catalysts.

Figure 4a shows TCM conversion upon time on stream with the catalysts tested at 0.2 kg·h·mol⁻¹ space time. All the catalysts yielded complete initial TCM conversion, but displayed very important differences in their deactivation trends. The most stable was ZnCPd, which did not show any significant reduction of TCM conversion (< 2%) after 52 hours of reaction. In contrast, FeCPd suffered a dramatic deactivation after few hours on stream and then a low residual activity was maintained. This deactivation can be associated to the deposition of by-products since the carbon unbalance reached 12 %²⁸⁻³⁰. The other three catalysts showed also a clear monotonical deactivation, although at lower rate. In all the cases, a quite stable selectivity to olefins was observed (see Figure 4b). That selectivity followed the order FeCPd > ZnCPd > KCPd ≈ NaCPd > PCPd. The two first yielded significant values of selectivity to olefins (62 and 55%, respectively)

during the 50-h on stream experiments. Therefore, the ZnCPd is by far the best-performance catalyst for olefins production upon TCM hydrodechlorination. Table 1 summarizes, in more detail, the selectivity values to the different reaction products. As can be seen, at the space time used in the experiments, a complete dechlorination was not achieved, although with the best catalysts, ZnCPd, almost a 93 % conversion was reached, while the rest remaining far below that value. The olefins produced were ethylene and propylene, being the first main reaction product in all cases except with the PCPd catalyst, which was much more selective toward methane.

The N₂ adsorption-desorption isotherms at -196 °C of the different catalysts before and after use in a long-term test (50 h on stream) are given in Figure S4 of supporting information. All the isotherms correspond to essentially (FeCPd, NaCPd, and KCPd) or predominantly (PCPd and ZnCPd) microporous solids. The last two include a significant contribution of mesoporosity, most in particular ZnCPd. After use, the shape of the respective isotherms did not change but the N₂ uptake decreased quite significantly, thus indicating a partial blockage of the initial porosity, which must be due to surface coverage by deposition of species involved in the reaction, including possible coke formation. This is consistent with the C balances, which, although in different extents, were never closed. Table 2 summarizes the BET surface area, A_{BET}, and the external surface area, A_{EXT}, of the fresh and used catalysts. All the catalysts show high BET surface area values, although with significant differences associated to the nature of the corresponding carbon supports prepared with different activating agents. The most stable catalyst, ZnCPd, is also the one with more open and widely distributed porous texture, which is expected to get less blockage of active sites since it has substantially higher external, or non-micropore area.

Table 3 displays the amount of CO and CO₂ desorbed from the catalysts upon TPD. Activation with alkaline agents produced significantly higher amount of oxygen groups, on the surface of the carbon support. In all cases, much higher amount of CO was evolved, this being associated mostly with oxygen groups of basic, or weakly acid character. The ZnCPd and FeCPd catalysts, showing lower amounts of surface oxygen groups, yielded also higher selectivities to olefins (see Table 1). The catalysts with higher amounts of these groups showed deep deactivation which can be associated with enhanced adsorption of reactants and/or reaction products. The strong deactivation of FeCPd catalyst has a different origin, as it will be explained later in the text.

Table 3 includes the assessment of surface CO₂- and CO-evolving groups from the deconvolution of the TPD profiles (Figures S5 and S6), according to literature criteria^{31–33}. Besides the lower amount of total oxygen groups observed for ZnCPd and FeCPd, the more remarkable difference is the absence, or very small amount of carbonyl/quinone groups in these catalysts. The presence of these groups may promote hydrogenation reactions by favouring adsorption of reactants and thus reaction with the surrounding H₂^{34–36}. The high concentrations of the aforementioned groups on the surface of NaCPd and KCPd catalysts may enhance the extent of hydrogenation of the adsorbed radicals leading to a higher proportion of ethane and propane instead of ethylene and propylene (Table 1). PCPd, with the highest amount of CO evolving groups, allowed the highest hydrogenation extent and the lower selectivity to olefins. However, the poor performance of PCPd for chloromethanes coupling (Table 1) can be explained by the presence of C-O-P surface groups providing very strong acid sites, as it was found in a previous work³², due to the remaining phosphorous from the activating agent. The formation of these surface groups, which decompose to CO at high temperature, and their implication in the formation of strong acid sites has been previously reported by other authors^{32,33,37–39}.

The catalysts surface composition and palladium oxidation state of reduced and used catalysts was analysed by XPS and the results are summarized in Table 4. The reduced fresh catalysts show two species of Pd, a $\text{Pd}3d_{5/2}$ peak centered at approximately 335.5 eV which can be assigned to Pd^0 (metallic Pd), and other lying near 338.0 eV corresponding to Pd^{n+} (electrodeficient palladium) ^{40,41} (Figure S7). The different concentration of oxygen functional groups on the surface, seems to have a direct implication on the Pd oxidation state. Correlation between the total amount of $\text{CO}+\text{CO}_2$ released and the $\text{Pd}^{n+}/\text{Pd}^0$ ratio can be seen in Figure 5. The interaction of Pd precursor with surface oxygen groups may lead to an increase of electro-deficient Pd as suggested by Figure 5. Except for PCPd, the behaviour of which appears to be affected by the presence of strong acid sites derived from phosphorus surface groups, the selectivity to olefins is enhanced at increasing $\text{Pd}^0/\text{Pd}^{n+}$ ratio.

The analysis of the catalysts after the reaction shows a decrease of zero-valent Pd for KCPd, NaCPd and FeCPd, while in ZnCPd this proportion increases, contributing to the reactivation of the catalyst at the highest time on stream tested ⁴² (Figure 4). On the other hand, an increase of organic chlorine on the surface of the catalysts was observed after reaction (Table 4), more pronounced in KCPd and NaCPd. An example of the deconvolution of $\text{Cl}2p$ spectra is shown in Figure S8. Poisoning of active centres by chlorocarbon seems to occur, as previously was found for other Pd/C catalysts ^{43–47}. A molecular simulation study ³⁰ showed that electro-deficient species favour non-dissociative adsorption of chloromethanes. The high amount of $\cdot\text{Cl}$ on the used KCPd and NaCPd catalysts suggests that the presence of CO evolving groups promotes irreversible chemisorption of chlorocarbons. Moreover, deconvolution of $\text{Pd}3d_{5/2}$ for these two

catalysts suggests the formation of palladium carbide species^{46,47} which may contribute to deactivation of the catalysts (Figure S9).

A significant decrease in concentration of surface Pd is observed except for FeCPd where the opposite occurred (Table 4). Besides the important decrease of surface area of PCPd after use, the reduction of Pd content (Table 4) supports the conclusion that deactivation of this catalyst takes place mainly by the blockage of metallic active sites by carbonaceous deposits. TCM conversion decreased more markedly at the end of the long-time experiment (Figure 4.a) and formation of deposits is probably promoted by the strong acid surface sites as identified in previous work^{25,32,33,48,49}. By contrast, the FeCPd used catalyst showed an increase of surface Pd, and the relative amount of Pdⁿ⁺ species, with reduction of surface Fe content observed by XPS (not shown) that suggest migration and modification of oxidation state of Pd particles during the reaction by the interaction with the reactants. However, the catalyst could be regenerated after treatment with a flow of air of 50 cm³min⁻¹ at 300 °C during 12 h. The conversion level and complete selectivity to olefins were recovered after this treatment.

Figure S10 shows the XRD pattern of the five catalysts prior and after use. Metallic Fe with peaks at 44.4°, 64.8° and 82.1° is the main phase identified on the reduced fresh catalyst. Peaks at 31.0°, 35.2°, 42.9°, and between 53.0° and 62.5° can be ascribed to FeO, which disappear after reduction at 350 °C (not shown). The presence of FePd particles cannot be discarded since they share diffraction angle with Fe. After reaction, the most significant modification is the disappearance of Fe peaks, besides the increase of the intensity and the shift to a higher scattering angle of the metallic Pd signal. In addition, new Fe phases were identified. The results suggest a significant modification and sintering of active centres, which can be attributed to the interaction with the chlorinated atmosphere, leading to strong deactivation of the catalyst.

The XRD patterns of the fresh KCPd reduced at 300 °C and after 50 hours on stream show only two peaks at 28.2° and 40.3° corresponding to KCl⁵⁰. The absence of Pd diffraction peaks suggests that the metallic phase is highly dispersed, without sintering during the reaction. The wide bands at 22° and 43° correspond to turbostratic carbon phase, graphite-like layered structure, but without the 3-D crystal structure of graphite⁵¹. This phase is commonly observed in chemical synthesis working at high temperatures (≥ 500 °C)^{52–54}. NaCPd patterns also show NaCl phases (Figure S10). However, unlike in the case of KCPd, now peaks associated with metallic Pd can be seen with a shift to higher scattering angle after reaction. This may indicate the formation of Pd carbide species^{42,46}, in agreement with the XPS results. The formation of these species was found to cause the deactivation of Pd catalysts in previous studies^{46,47}. No diffraction peaks were found in the patterns of ZnCPd and PCPd catalysts (Figure S10), suggesting a good dispersion of Pd.

The Pd particle size distribution were obtained from TEM images (Figure 6). The FeCPd catalysts show Fe clusters clearly visible. In the fresh reduced catalyst those clusters have a mean particle size of 60 nm. No presence of Pd was observed by EDX, indicating that Pd particles are very small (smaller than the 2 nm, resolution limit of the microscope), or surrounded by huge Fe and FeO clusters or big aisle agglomerates, that makes difficult to see them by TEM. After HDC, sintering of Fe clusters can be observed. These Fe aggregates have been confirmed by XRD and are typical of particles with magnetic properties, as Fe/FeO. The mean particle size for the fresh and the used KCPd catalyst were 5.4 and 3.8 nm respectively. No sintering of Pd particles was observed after reaction, in contrast, some re-dispersion seems to have occurred. Small and well distributed Pd particles and those of sizes up to 20 nm are observed for the fresh NaCPd catalyst, with a mean particle size of 7.9 nm. Comparison with XRD results suggests that this catalyst

exhibits a great heterogeneity of Pd particle size. On the other hand, considerably larger particles (30.0 nanometres of mean particle size) are seen in the used one. However, this feature does not seem to have a significant effect on the performance of this catalyst, which is more remarkably influenced by the metal oxidation state and surface carbon chemistry.

ZnCPd undergo a redispersion of Pd particles after HDC reaction. Mean particle sizes of 10.0 and 2.7 nm were measured for the fresh-reduced and used catalysts, respectively. This re-dispersion has been widely reported in the literature, which can take place in chlorine environment at moderate temperatures, depending on the nature of the support, the metallic phase and chlorine concentration^{55–57}. In former hydrodechlorination studies, small particle sizes were found to prevent deactivation of metallic catalysts avoiding the oligomerization of carbonaceous species and subsequent poisoning of active centres^{46,58}. The excellent stability of the ZnCPd catalyst appears to be a consequence of the combination of an optimum surface chemistry and metal particle size. A mean particle size of 3 nm was measured in the used PCPd catalyst. This is consistent with XRD and confirm that the deep deactivation of this catalyst is not due to metal particles sintering but to its surface chemistry and acidity.

Since ZnCPd and FeCPd based catalysts showed the highest selectivity to olefins but very different stability, additional STEM characterization of the used catalysts was carried out to confirm their differences on Pd particle sizes. The STEM images are given in Figure 7. ZnCPd showed very small Pd nanoparticles homogeneously distributed over the surface of the support, with a mean particle size of 2.3 nm. The analysis revealed that they were only composed of Pd. In contrast, FeCPd showed very few Pd nanoparticles of 30 nm in size and above. The analyses yielded 97.5 % (atomic) Pd, and 2.49 % of Fe, suggesting the formation of bimetallic particles or an alloy under the reaction conditions.

These findings support the observed high, and low stability of ZnCPd and FeCPd catalysts, respectively.

Conclusions

Ethylene and propylene can be selectively obtained from the hydrodechlorination of chloroform at suitable reaction conditions (H_2 /TCM molar ratio of 50 and reaction temperature of 300 °C), by using Pd catalysts on carbon supports prepared by activation of lignin with $ZnCl_2$ and $FeCl_3$. All the catalysts used in this study showed high TCM conversion, but the yield to olefins and the stability of the catalysts varied greatly depending on their surface properties. The use of different agents to activate lignin confers to the support a distinct morphology and the concentration and composition of surface CO and CO_2 evolving groups. These variations result in different Pd electro-deficiency and metal particle size distribution. There is a correlation between the amount of surface oxygenated groups and the proportion of Pd^{n+} in the catalysts. The presence of these groups and Pd species appears to promote the complete hydrogenation of reaction intermediates, as they favour a strong adsorption of reactants, leading to a higher selectivity to alkanes. Furthermore, they promote the deactivation of the catalysts because of the poisoning of active centres by chemisorption of chlorocarbon compounds. In contrast, $ZnCl_2$, and $FeCl_3$ derived catalysts, with the higher proportion of zero-valent Pd and lower amount of surface oxygen functional groups render the highest selectivity to olefins. However, the presence of Fe particles on the surface of $FeCl_3$ derived catalyst and its high microporosity promotes sintering of Pd particles and the blockage of active centres by carbon deposition, which in turn lead to a strong deactivation of the catalyst during the HDC reaction. The weaker interaction of Pd particles with the support on $ZnCl_2$ derived catalyst (as a consequence of the significant contribution of mesoporosity), in

addition to the low amount of surface oxygen functional groups on the surface, lead to the re-dispersion of the active phase during the reaction. Thus, the formation of very small and homogeneously distributed Pd particles prevents the deactivation of the catalyst and results in a high selectivity to olefins.

Acknowledgements

Authors acknowledge financial support from FEDER/Ministerio de Ciencia, Innovación y Universidades – Agencia Estatal de Investigación/ CTM2017-85498-R. C. Fernández Ruiz acknowledges MINECO for his research grant. S. Andreoli acknowledges the fellowship received from “Toso Montanari” foundation, University of Bologna.

Supplementary Materials

Supplementary information provide conversion and selectivity results of KCPd catalyst at different reduction temperatures and different H₂/TCM molar ratios. CO₂ and CO TPD deconvoluted profiles of fresh reduced catalysts is also included in supplementary materials, in addition to the following information relative to the catalysts fresh reduced and used in the reaction: isotherms obtained from N₂ adsorption-desorption, XPS Pd3d and Cl2p deconvolution spectra and XRD patterns.

References

- (1) Arevalo-Bastante, A.; Álvarez-Montero, M. A.; Bedia, J.; Gómez-Sainero, L. M.; Rodriguez, J. J. Gas-Phase Hydrodechlorination of Mixtures of Chloromethanes with Activated Carbon-Supported Platinum Catalysts. *Appl. Catal. B Environ.* **2015**, *179*, 551–557. <https://doi.org/10.1016/j.apcatb.2015.05.058>.
- (2) Mcculloch, A. Chloroform in the Environment - Occurrence, Sources, Sinks and Effects. **2002**.
- (3) Amghizar, I.; Vandewalle, L. A.; Geem, K. M. Van; Marin, G. B. New Trends in Olefin Production. *Engineering* **2017**, *3* (2), 171–178. <https://doi.org/10.1016/J.ENG.2017.02.006>.
- (4) BP. Methodological Changes. *Stat. Rev. World Energy* **2018**, 1–56.
- (5) Darvishi, A.; Davand, R.; Khorasheh, F.; Fattahi, M. Modeling-Based Optimization of a Fixed-Bed Industrial Reactor for Oxidative Dehydrogenation of Propane. *Chinese J. Chem. Eng.* **2016**, *24* (5), 612–622. <https://doi.org/10.1016/j.cjche.2015.12.018>.
- (6) Batamack, P. T. D.; Mathew, T.; Prakash, G. K. S. One-Pot Conversion of Methane to Light Olefins or Higher Hydrocarbons through H-SAPO-34-Catalyzed in Situ Halogenation. *J. Am. Chem. Soc.* **2017**, *139* (49), 18078–18083. <https://doi.org/10.1021/jacs.7b10725>.
- (7) Lin, R.; Amrute, A. P.; Pérez-Ramírez, J. Halogen-Mediated Conversion of Hydrocarbons to Commodities. *Chem. Rev.* **2017**, *117* (5), 4182–4247. <https://doi.org/10.1021/acs.chemrev.6b00551>.
- (8) McFarland, E. Unconventional Chemistry for Unconventional Natural Gas.

- Science* (80-.). **2012**, 338 (6105), 341–342.
<https://doi.org/10.1126/science.1226840>.
- (9) Paunovic, V.; Zichittella, G.; Moser, M.; Amrute, A. P.; Pérez-Ramírez, J. Catalyst Design for Natural-Gas Upgrading through Oxybromination Chemistry. *Nat. Chem.* **2016**, 8 (8), 803–809. <https://doi.org/10.1038/nchem.2522>.
- (10) Rhodes, W. D.; Kovalchuk, V. I.; McDonald, M. A. Reaction Pathways of Halocarbon Catalytic Oligomerization. *Catal. Commun.* **2012**, 18, 98–101.
<https://doi.org/10.1016/j.catcom.2011.11.019>.
- (11) Golubina, E. V.; Lokteva, E. S.; Lazareva, T. S.; Kostyuk, B. G.; Lunin, V. V.; Simagina, V. I.; Stoyanova, I. V. Hydrodechlorination of Tetrachloromethane in the Vapor Phase in the Presence of Pd-Fe/Sibunit Catalysts. *Kinet. Catal.* **2004**, 45 (2), 183–188. <https://doi.org/10.1023/B:KICA.0000023789.28190.1b>.
- (12) Lokteva, E. S.; Simagina, V. I.; Golubina, E. V.; Stoyanova, I. V.; Lunin, V. V. Formation of C 1 –C 5 Hydrocarbons from CCl 4 in the Presence of Carbon-Supported Palladium Catalysts. *Kinet. Catal.* **2000**, 41 (6), 776–781.
<https://doi.org/10.1023/A:1026621102928>.
- (13) Svelle, S.; Aravinthan, S.; Bjørgen, M.; Lillerud, K. P.; Kolboe, S.; Dahl, I. M.; Olsbye, U. The Methyl Halide to Hydrocarbon Reaction over H-SAPO-34. *J. Catal.* **2006**, 241 (2), 243–254. <https://doi.org/10.1016/j.jcat.2006.04.013>.
- (14) Wei, Y.; Zhang, D.; Xu, L.; Liu, Z.; Su, B. L. New Route for Light Olefins Production from Chloromethane over HSAPO-34 Molecular Sieve. *Catal. Today* **2005**, 106 (1–4), 84–89. <https://doi.org/10.1016/j.cattod.2005.07.142>.
- (15) Wei, Y.; Zhang, D.; Liu, Z.; Su, B. L. Highly Efficient Catalytic Conversion of

- Chloromethane to Light Olefins over HSAPO-34 as Studied by Catalytic Testing and in Situ FTIR. *J. Catal.* **2006**, *238* (1), 46–57.
<https://doi.org/10.1016/j.jcat.2005.11.021>.
- (16) Yang, Y.; He, Y.; Liu, Z.; Xu, L.; Su, B.-L.; Wei, Y.; Zhang, D. Catalytic Performance of Chloromethane Transformation for Light Olefins Production over SAPO-34 with Different Si Content. *Catal. Letters* **2007**, *114* (1–2), 30–35.
<https://doi.org/10.1007/s10562-007-9038-4>.
- (17) Olsbye, U.; Saure, O. V.; Muddada, N. B.; Bordiga, S.; Lamberti, C.; Nilsen, M. H.; Lillerud, K. P.; Svelle, S. Methane Conversion to Light Olefins - How Does the Methyl Halide Route Differ from the Methanol to Olefins (MTO) Route? *Catal. Today* **2011**, *171* (1), 211–220.
<https://doi.org/10.1016/j.cattod.2011.04.020>.
- (18) Śrebowata, A.; Juszczak, W.; Kaszkur, Z.; Karpiński, Z. Hydrodechlorination of 1,2-Dichloroethane on Active Carbon Supported Palladium-Nickel Catalysts. *Catal. Today* **2007**, *124* (1–2), 28–35.
<https://doi.org/10.1016/j.cattod.2007.02.010>.
- (19) Hannus, I.; Halász, J. Hydrodechlorination over Zeolite □Supported Catalysts: Clarification of the Reaction Mechanism. *J. Japan Pet. Inst.* **2007**, *49* (3), 105–113. <https://doi.org/https://doi.org/10.1627/jpi.49.105>.
- (20) Meshesha, B. T.; Barrabés, N.; Föttinger, K.; Chimentão, R. J.; Llorca, J.; Medina, F.; Rupprechter, G.; Sueiras, J. E. Gas-Phase Hydrodechlorination of Trichloroethylene over Pd/NiMgAl Mixed Oxide Catalysts. *Appl. Catal. B Environ.* **2012**, *117–118*, 236–245. <https://doi.org/10.1016/j.apcatb.2012.01.018>.
- (21) Śrebowata, A.; Baran, R.; Słowik, G.; Lisovytskiy, D.; Dzwigaj, S. Influence of

- the Postsynthesis Preparation Procedure on Catalytic Behaviour of Ag-Loaded BEA Zeolites in the Hydrodechlorination of 1,2-Dichloroethane into Value Added Products. *Appl. Catal. B Environ.* **2016**, *199*, 514–522.
<https://doi.org/10.1016/j.apcatb.2016.06.060>.
- (22) Śrębowata, A.; Kamińska, I. I.; Casale, S.; Brouri, D.; Calers, C.; Dzwigaj, S. The Impact of the Hydrodechlorination Process on the Physicochemical Properties of Bimetallic Ag-CuBeta Zeolite Catalysts. *Microporous Mesoporous Mater.* **2017**, *243*, 56–64. <https://doi.org/10.1016/j.micromeso.2016.12.022>.
- (23) Han, Y.; Sun, J.; Fu, H.; Qu, X.; Wan, H.; Xu, Z.; Zheng, S. Highly Selective Hydrodechlorination of 1,2-Dichloroethane to Ethylene over Ag-Pd/ZrO₂ Catalysts with Trace Pd. *Appl. Catal. A Gen.* **2016**, *519*, 1–6.
<https://doi.org/10.1016/j.apcata.2016.03.017>.
- (24) Gómez-Sainero, L. M.; Palomar, J.; Omar, S.; Fernández, C.; Bedia, J.; Álvarez-Montero, A.; Rodriguez, J. J. Valorization of Chloromethanes by Hydrodechlorination with Metallic Catalysts. *Catal. Today* **2017**, No. February, 1–11. <https://doi.org/10.1016/j.cattod.2017.05.006>.
- (25) Fernandez-Ruiz, C.; Bedia, J.; Bonal, P.; Rodriguez, J. J.; Gómez-Sainero, L. M. Chloroform Conversion into Ethane and Propane by Catalytic Hydrodechlorination with Pd Supported on Activated Carbons from Lignin. *Catal. Sci. Technol.* **2018**, *8* (15), 3926–3935.
<https://doi.org/10.1039/c8cy00461g>.
- (26) Job, N.; Heinrichs, B.; Ferauche, F.; Noville, F.; Marien, J.; Pirard, J. P. Hydrodechlorination of 1,2-Dichloroethane on Pd-Ag Catalysts Supported on Tailored Texture Carbon Xerogels. *Catal. Today* **2005**, *102–103* (3), 234–241.

- <https://doi.org/10.1016/j.cattod.2005.02.021>.
- (27) Kinetics, I. I. I.; Mechanism, R. Palladium – Silver Sol – Gel Catalysts for Selective Hydrodechlorination of 1, 2-Dichloroethane into Ethylene. **2001**, 320, 309–320. <https://doi.org/10.1006/jcat.2001.3188>.
- (28) Zhang, Q.; Lü, J.; Ma, L.; Lu, C.; Liu, W.; Li, X. Study on Deactivation by Sulfur and Regeneration of Pd/C Catalyst in Hydrogenation of N-(3-Nitro-4-Methoxyphenyl) Acetamide. *Chinese J. Chem. Eng.* **2013**, 21 (6), 622–626. [https://doi.org/10.1016/S1004-9541\(13\)60497-8](https://doi.org/10.1016/S1004-9541(13)60497-8).
- (29) Álvarez-Montero, M. A.; Rodriguez, J. J.; Gómez-Sainero, L. M. Platinum Nanoparticles Supported on Activated Carbon Catalysts for the Gas-Phase Hydrodechlorination of Dichloromethane: Influence of Catalyst Composition and Operating Conditions. *Nanomater. Nanotechnol.* **2016**, 1. <https://doi.org/10.5772/62593>.
- (30) Omar, S.; Palomar, J.; Gómez-Sainero, L. M.; Álvarez-Montero, M. A.; Martin-Martinez, M.; Rodriguez, J. J. Density Functional Theory Analysis of Dichloromethane and Hydrogen Interaction with Pd Clusters: First Step to Simulate Catalytic Hydrodechlorination. *J. Phys. Chem. C* **2011**, 115 (29), 14180–14192. <https://doi.org/10.1021/jp200329j>.
- (31) Figueiredo, J. .; Pereira, M. F. .; Freitas, M. M. .; Órfão, J. J. . Modification of the Surface Chemistry of Activated Carbons. *Carbon N. Y.* **1999**, 37 (9), 1379–1389. [https://doi.org/10.1016/S0008-6223\(98\)00333-9](https://doi.org/10.1016/S0008-6223(98)00333-9).
- (32) Rosas, J. M.; Bedia, J.; Rodríguez-Mirasol, J.; Cordero, T. Preparation of Hemp-Derived Activated Carbon Monoliths. Adsorption of Water Vapor. *Ind. Eng. Chem. Res.* **2008**. <https://doi.org/10.1021/ie070924w>.

- (33) Rosas, J. M.; Bedia, J.; Rodríguez-Mirasol, J.; Cordero, T. HEMP-Derived Activated Carbon Fibers by Chemical Activation with Phosphoric Acid. *Fuel* **2009**. <https://doi.org/10.1016/j.fuel.2008.08.004>.
- (34) Castillejos, E.; García-Minguillán, A. M.; Bachiller-Baeza, B.; Rodríguez-Ramos, I.; Guerrero-Ruiz, A. When the Nature of Surface Functionalities on Modified Carbon Dominates the Dispersion of Palladium Hydrogenation Catalysts. *Catal. Today* **2018**, *301* (April), 248–257. <https://doi.org/10.1016/j.cattod.2017.05.024>.
- (35) An, N.; Zhang, M.; Zhang, Z.; Dai, Y.; Shen, Y.; Tang, C.; Yuan, X.; Zhou, W. High-Performance Palladium Catalysts for the Hydrogenation toward Dibenzylbiotinmethylester: Effect of Carbon Support Functionalization. *J. Colloid Interface Sci.* **2018**, *510*, 181–189. <https://doi.org/10.1016/j.jcis.2017.09.014>.
- (36) Guo, Y.; Li, Y.; Zhu, T.; Wang, J.; Ye, M. Modeling of Dioxin Adsorption on Activated Carbon. *Chem. Eng. J.* **2016**, *283*, 1210–1215. <https://doi.org/10.1016/j.cej.2015.08.067>.
- (37) Bedia, J.; Rosas, J. M.; Márquez, J.; Rodríguez-Mirasol, J.; Cordero, T. Preparation and Characterization of Carbon Based Acid Catalysts for the Dehydration of 2-Propanol. *Carbon N. Y.* **2009**. <https://doi.org/10.1016/j.carbon.2008.10.008>.
- (38) Valero-Romero, M. J.; García-Mateos, F. J.; Rodríguez-Mirasol, J.; Cordero, T. Role of Surface Phosphorus Complexes on the Oxidation of Porous Carbons. *Fuel Process. Technol.* **2017**, *157*, 116–126. <https://doi.org/10.1016/j.fuproc.2016.11.014>.

- (39) Ruiz-Rosas, R.; García-Mateos, F. J.; Gutiérrez, M. del C.; Rodríguez-Mirasol, J.; Cordero, T. About the Role of Porosity and Surface Chemistry of Phosphorus-Containing Activated Carbons in the Removal of Micropollutants. *Front. Mater.* **2019**. <https://doi.org/10.3389/fmats.2019.00134>.
- (40) Gómez-Sainero, L. M.; Baker, R. T.; Metcalfe, I. S.; Sahibzada, M.; Concepción, P.; López-Nieto, J. M. Investigation of Sm₂O₃-CeO₂-Supported Palladium Catalysts for the Reforming of Methanol: The Role of the Support. *Appl. Catal. A Gen.* **2005**, *294* (2), 177–187. <https://doi.org/10.1016/j.apcata.2005.07.022>.
- (41) Gómez-Sainero, L. M.; Grau, J. M.; Arcoya, A.; Seoane, X. L. Carbon-Supported Palladium Catalysts for Liquid-Phase Hydrodechlorination of Carbon Tetrachloride to Chloroform. **2007**, 2009–2014. [https://doi.org/10.1016/s0167-2991\(00\)80763-6](https://doi.org/10.1016/s0167-2991(00)80763-6).
- (42) Liu, S.; Martin-Martinez, M.; Álvarez-Montero, M. A.; Arevalo-Bastante, A.; Rodriguez, J. J.; Gómez-Sainero, L. M. Recycling of Gas Phase Residual Dichloromethane by Hydrodechlorination: Regeneration of Deactivated Pd/C Catalysts. *Catalysts* **2019**, *9* (9), 733. <https://doi.org/10.3390/catal9090733>.
- (43) Yuan, G.; Keane, M. A. Role of Base Addition in the Liquid-Phase Hydrodechlorination of 2,4-Dichlorophenol over Pd/Al₂O₃ and Pd/C. *J. Catal.* **2004**, *225* (2), 510–522. <https://doi.org/10.1016/j.jcat.2004.05.003>.
- (44) Janiak, T.; Okal, J. Effectiveness and Stability of Commercial Pd/C Catalysts in the Hydrodechlorination of Meta-Substituted Chlorobenzenes. *Appl. Catal. B Environ.* **2009**, *92* (3–4), 384–392. <https://doi.org/10.1016/j.apcatb.2009.08.018>.
- (45) Martin-Martinez, M.; Gómez-Sainero, L. M.; Alvarez-Montero, M. A.; Bedia, J.; Rodriguez, J. J. Comparison of Different Precious Metals in Activated Carbon-

- Supported Catalysts for the Gas-Phase Hydrodechlorination of Chloromethanes. *Appl. Catal. B Environ.* **2013**, *132–133*, 256–265.
<https://doi.org/10.1016/j.apcatb.2012.11.041>.
- (46) Martin-Martinez, M.; Álvarez-Montero, A.; Gómez-Sainero, L. M.; Baker, R. T.; Palomar, J.; Omar, S.; Eser, S.; Rodriguez, J. J. Deactivation Behavior of Pd/C and Pt/C Catalysts in the Gas-Phase Hydrodechlorination of Chloromethanes: Structure-Reactivity Relationship. *Appl. Catal. B Environ.* **2015**, *162*, 532–543.
<https://doi.org/10.1016/j.apcatb.2014.07.017>.
- (47) Álvarez-Montero, M. A.; Gómez-Sainero, L. M.; Juan-Juan, J.; Linares-Solano, A.; Rodriguez, J. J. Gas-Phase Hydrodechlorination of Dichloromethane with Activated Carbon-Supported Metallic Catalysts. *Chem. Eng. J.* **2010**, *162* (2), 599–608. <https://doi.org/10.1016/j.cej.2010.06.002>.
- (48) Magnacca, G.; Morterra, C. A Case Study: Surface Chemistry and Surface Structure of Catalytic Aluminas, as Studied by Vibrational Spectroscopy of Adsorbed Species. *Catal. Today* **1996**, *27* (3–4), 497–532.
[https://doi.org/10.1016/0920-5861\(95\)00163-8](https://doi.org/10.1016/0920-5861(95)00163-8).
- (49) BERTEAU, P.; KELLENS, M.-A.; DELMON, B. Acid-Base Properties of Modified Aluminas. *J. Chem. Soc. Faraday Trans.* **1991**, *87* (9), 1425–1431.
<https://doi.org/10.1039/FT9918701425>.
- (50) Wang, W. L.; Ren, X. Y.; Chang, J. M.; Cai, L. P.; Shi, S. Q. Characterization of Bio-Oils and Bio-Chars Obtained from the Catalytic Pyrolysis of Alkali Lignin with Metal Chlorides. *Fuel Process. Technol.* **2015**, *138*, 605–611.
<https://doi.org/10.1016/j.fuproc.2015.06.048>.
- (51) Ruz, P.; Banerjee, S.; Pandey, M.; Sudarsan, V.; Sastry, P. U.; Kshirsagar, R. J.

- Structural Evolution of Turbostratic Carbon: Implications in H₂storage. *Solid State Sci.* **2016**, *62*, 105–111.
<https://doi.org/10.1016/j.solidstatesciences.2016.10.017>.
- (52) Thambiliyagodage, C. J.; Ulrich, S.; Araujo, P. T.; Bakker, M. G. Catalytic Graphitization in Nanocast Carbon Monoliths by Iron, Cobalt and Nickel Nanoparticles. *Carbon N. Y.* **2018**, *134*, 452–463.
<https://doi.org/10.1016/j.carbon.2018.04.002>.
- (53) Chen, W.; Shi, S.; Nguyen, T.; Chen, M.; Zhou, X. Effect of Temperature on the Evolution of Physical Structure and Chemical Properties of Bio-Char Derived from Co-Pyrolysis of Lignin with High-Density Polyethylene. *BioResources* **2016**, *11* (2), 3923–3936. <https://doi.org/10.15376/biores.11.2.3923-3936>.
- (54) Mondal, S.; Elkamel, A.; Reinalda, D.; Wang, K. Preparation and Morphology Study of Carbon Molecular Sieve Membrane Derived from Polyimide. *Can. J. Chem. Eng.* **2017**, *95* (10), 1993–1998. <https://doi.org/10.1002/cjce.22881>.
- (55) C. Feeley, O.; Sachtler, W. M. H. Redispersion of Palladium in Y-Zeolites by Chlorine. *Appl. Catal.* **1991**, *75* (1), 93–103. [https://doi.org/10.1016/S0166-9834\(00\)83126-7](https://doi.org/10.1016/S0166-9834(00)83126-7).
- (56) Kim, S.; D’Aniello, M. J. Electron Microscopy Study of a Rejuvenated Vehicle-Aged Automotive Exhaust Catalyst. *Appl. Catal.* **1989**, *56* (1), 45–56.
[https://doi.org/10.1016/S0166-9834\(00\)80157-8](https://doi.org/10.1016/S0166-9834(00)80157-8).
- (57) Lambrou, P. S.; Polychronopoulou, K.; Petallidou, K. C.; Efstathiou, A. M. Oxy-Chlorination as an Effective Treatment of Aged Pd/CeO₂-Al₂O₃ catalysts for Pd Redispersion. *Appl. Catal. B Environ.* **2012**, *111–112*, 349–359.
<https://doi.org/10.1016/j.apcatb.2011.10.018>.

- (58) Álvarez-Montero, M. A.; Gómez-Sainero, L. M.; Mayoral, A.; Diaz, I.; Baker, R. T.; Rodriguez, J. J. Hydrodechlorination of Chloromethanes with a Highly Stable Pt on Activated Carbon Catalyst. *J. Catal.* **2011**, 279 (2), 389–396.
<https://doi.org/10.1016/j.jcat.2011.02.009>.

Table 1. TCM conversion, selectivity and dechlorination degree after 50 h on stream(reaction temperature = 300 °C; τ = 0.2 kg h mol⁻¹; H₂/TCM molar ratio = 50).

	Conversion (%)	Selectivity (%)						Dechlorination (%)
	X _{TCM}	CH ₄	C ₂ H ₆	C ₂ H ₄	C ₃ H ₈	C ₃ H ₆	DCM	
ZnCPd	98	14	17	39	3	16	8	92.8
PCPd	37	63	1	20	0	3	13	33.8
FeCPd	19	26	7	53	1	9	2	18.7
KCPd	47	16	32	25	10	9	2	46.4
NaCPd	31	17	33	27	9	8	1	30.8

Table 2. Porous texture parameters of the fresh and used catalysts after 50 h reaction.

Catalyst	A _{BET} (m ² ·g ⁻¹)		A _{ext} (m ² g ⁻¹)	
	Fresh catalysts	Used catalysts	Fresh catalysts	Used catalysts
FeCPd	852	435	55	33
ZnCPd	1103	695	709	383
PCPd	732	409	406	233
NaCPd	2158	1942	108	172
KCPd	2991	2812	85	160

Table 3. Distribution of oxygen surface groups obtained by deconvolution of CO₂ and CO TPD profiles.

CO ₂ (μmol·g ⁻¹)	Catalyst				
	ZnCPd	FeCPd	NaCPd	KCPd	PCPd
Carboxylic acids	49.9	88.4	143.0	245.1	45.8
Lactones	25.0	74.4	136.0	231.3	7.9
Anhydrides	83.2	72.3	148.1	229.6	81.3
Total CO₂	158	235	427	706	135
CO (μmol·g ⁻¹)					
Aldehydes & Ketones	35.5	42.8	150.2	224.0	33.2
Anhydrides	83.2	71.3	165.2	227.0	81.8
Phenol	620.4	370.7	2703.3	771.8	417.6
Carbonyl & Quinone	--	71.3	300.4	363.2	491.2*
Total CO	739	556	3319	1586	1023
Total CO₂+CO	897	791	3746	2292	1158

*It can be additionally ascribed to C-O-P surface groups

Table 4. Pd and Cl mass surface concentration and Pd oxidation state obtained by deconvolution of the Pd3d XPS signal of the fresh and used catalysts.

Catalyst		% Pd (w.t.)	% Pd ⁰	% Pd ⁿ⁺	% PdC	% Cl (w.t.)
FeCPd	fresh	0.25	77	23	-	1.47
	used	1.24	58	42	-	5.67
ZnCPd	fresh	1.13	65	35	-	0.61
	used	0.68	72	28	-	1.85
PCPd	fresh	1.45	60	40	-	-
	used	0.47	61	39	-	9.89
NaCPd	fresh	0.62	48	52	-	1.37
	used	0.36	28	18	54	23.50
KCPd	fresh	0.95	47	53	-	0.92
	used	0.38	22	17	61	16.55

1
2
3
4
5
6
7

Figure 1. Evolution of the yield to olefins with reaction temperature at different H₂/TCM molar ratios (KCPd catalyst, $\tau = 0.2 \text{ kg h mol}^{-1}$).

Figure 2. Evolution of TCM conversion with reaction temperature on the different catalysts at the optimized conditions ($\tau = 0.2 \text{ kg h mol}^{-1}$, reduction temperature = 300 °C; H_2/TCM molar ratio = 50).

Figure 3. Evolution of selectivity to olefins and paraffins with reaction temperature ($\tau = 3$ 0.2 kg h mol⁻¹, H₂/TCM molar ratio = 50).

1

Figure 4. Evolution of (a) TCM conversion and (b) selectivity to olefins with time on stream ($\tau = 0.2 \text{ kg h mol}^{-1}$, reaction temperature = 300°C , H_2/TCM molar ratio = 50).

Figure 5. Pd^{n+}/Pd^0 ratio and CO + CO₂ evolved from TPDs of the different catalysts.

Figure 6. TEM images of the fresh and used catalysts.

Figure 7. STEM-HAADF of FeCPd and ZnCPd catalysts after 50 hours of time on stream.

GRAPHICAL ABSTRACT