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Gas-phase hydrodechlorination of mixtures of chloromethanes with activated carbon-supported platinum catalysts

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Abstract. Platinum catalysts supported on activated carbon (Pt/C) at different metal loadings (0.5-2% Pt) have been tested in the gas-phase hydrodechlorination (HDC) of mixtures of dichloromethane (DCM) and chloroform (TCM), with a total feed concentration of 1000 ppm_v. Almost complete dechlorination was achieved at 250 ºC, 1 $kg·h·mol^{-1}$ space time and a H_2/CM molar ratio of 25 with the 2% Pt catalyst. At a reaction temperature of 250 ºC, scarce inhibition in the conversion of both compounds was observed compared to the HDC of the individual chloromethanes. The TOF values for DCM increase with the Pt content, which can be attributed to the higher proportion of the zero-valent species. The selectivity to reaction products suggests a parallel reactions scheme. The catalysts showed a high stability, demonstrated by the unchanged conversion of both chloromethanes upon time on stream in long-term experiments carried out at up to 26 h.

Keywords: *hydrodechlorination, dichloromethane, chloroform, mixtures, Pt/C*

1. Introduction

The release of chloromethanes to the atmosphere represents a serious environmental problem. Chloromethanes (CMs) are chlorinated volatile organic compounds which are commonly used as solvents and reactants in numerous processes. They are also employed in the manufacture of aerosols, adhesives, and for dry cleaning [1]. The main problem of these compounds is their high toxicity and carcinogenic character. In addition to this, their emission contributes to the depletion of the ozone layer, global warming and the formation of photochemical smog [2-4]. In particular, dichloromethane (DCM) and chloroform (TCM) are included in the list of the 17 highly dangerous chemicals targeted in the emissions reduction effort of the US Environmental Protection Agency (EPA). In consequence, their emissions have been progressively submitted to more stringent regulations. This leads to the need of developing effective technologies for the treatment of residual streams contaminated with those species. Catalytic hydrodechlorination (HDC) is a suitable technology for this purpose since it can operate under ambient pressure and relative low temperature, the selectivity to reaction products can be modified, the reaction products are less dangerous than those obtained by other techniques and is applicable over a wide range of pollutant concentrations [5-7].

Several studies focused on the HDC of DCM or TCM have been published in the last years. However, in many cases, these CMs appear together in off-gas streams (for example in chloromethanes production plants [8]), and the application of HDC technology requires catalysts capable of working efficiently in those conditions [9]. There is scarce literature dealing with the HDC of mixtures of chlorinated compounds and the few studies available show reciprocal inhibitory effects which reduce the efficiency of the process compared with that found when working with each individual species. The main novelty of the current work lies on the study of HDC of mixtures of chloromethanes. Ordoñez et al. [10] analyzed the kinetics and the activity of a commercial Pd/Al_2O_3 catalyst in the simultaneous HDC of mixtures of tetrachloroethylene (TTCE), trichloroethylene (TCE) and 1,1-dichloroethylene (DCE). They found important inhibition phenomena since all of the organochlorinated compounds were adsorbed on the same active sites of the catalyst, as it was evidenced by the fitting to the kinetic models proposed. Gonzalez et al. [11] studied the HDC of mixtures of DCM, TCM and TTCE with Pd/TiO_2 catalysts, and observed much lower conversions than the obtained with the individual compounds. Furthermore, the catalysts showed deactivation by coke deposition and HCl poisoning. They also investigated the HDC of TCM and TTCE with DCM traces using palladium catalysts supported on alumina and titania [12], and found faster catalyst deactivation when working with mixtures of the three compounds.

The metallic active phase plays an important role in HDC. In previous studies [1, 13-16], we have investigated the HDC of individual chloromethanes (mainly DCM and TCM) using catalysts based on Pd, Pt, Rh and Ru supported on activated carbon. The catalysts were found to be effective in the HDC of DCM and TCM individually. However the efficiency of the process has not yet been proved with mixtures of both species where some possible inhibitory effects may occur. Although all the above mentioned metals showed effective in the HDC of the chloromethanes, significant differences were found in both, activity and selectivity. In all cases, high selectivities to non-chlorinated products (> 80%) were obtained, but the Pt/C catalyst showed much higher stability. Alvarez-Montero et al. [15] confirmed the exceptional stability of that catalyst with no loss of activity after 26 days on stream in the HDC of DCM. This was attributed to the different oxidation state of metallic particles on the catalytic surface and the smaller metal particle size. In contrast with other catalysts, in Pt/C the zero-valent species (Pt^0) predominated at the surface, which is more resistant to poisoning by chloromethane adsorption than the electro-deficient species (Pt^{n+}). On the other hand, redispersion of the active phase during the reaction was found, leading to much smaller metal particles, with a very homogeneous size distribution, well distributed over the support with very little agglomeration. The catalyst showed high conversion values (up to 95% conversion for DCM and 100% for TCM) and was highly selective to methane, which was the only non-chlorinated product (selectivities of up to 85% for HDC of DCM and 93% for HDC of TCM). Metal dispersion appeared to be a determining issue for the performance of these catalysts and usually it is modified depending on the metallic content. Moreover, the metal loading and dispersion are important factors to be considered. The effect of Pt loading in the HDC of these chloromethanes has not been previously studied.

The aim of this work is to analyze the performance of Pt/C catalysts with different Pt content (0.5-2%) in the gas phase HDC of mixtures of DCM and TCM.

2. Experimental

2.1. Catalysts preparation

Different platinum-containing catalysts supported on a commercial activated carbon (*Merck Carbon*) were prepared by incipient wetness impregnation, using aqueous solutions of $H_2PtCl_6 \cdot 6H_2O$ (supplied by Sigma-Aldrich) of appropriate concentration to obtain nominal Pt loadings in the range of 0.5 – 2.0 wt%. The activated carbon was used with a particle size of 0.25 – 0.50 mm. The catalysts were dried overnight at room temperature and heated up to 100 ºC at a rate of 20 $ºC \cdot h^{-1}$, maintaining the final temperature for 2 h. Finally, the activation of the catalysts was carried out by reduction under a continuous flow of H_2 (supplied by Praxair with a minimum purity of 99.999%) at 300 ºC for 2 h. A heating rate of 10 $ºC \cdot min^{-1}$ was used to reach the activation temperature.

2.2. Catalyst characterization

The porous structure of the catalysts was characterized by N_2 adsorption-desorption at -196 ºC (Tristar II 3020, Micromeritics). The samples were previously outgassed for 12 h at 150 ºC at a residual pressure of 10^{-3} Torr (VacPrep 061, Micromeritics). The surface areas were calculated by the BET equation and the t-method was used to obtain the micropore volume and the external or non-microporous surface area.

The bulk platinum content was determined via inductively coupled plasma-mass spectroscopy (ICP-MS) in an Elan 6000 PerkinElmer Sciex system, equipped with an autosampler AS-91. The samples were previously digested for 15 min with a strongly acidic mixture in a microwave oven (Milestone ETHOS PLUS) at 180 ºC.

The surface composition of the reduced catalysts was analyzed by X-ray photoelectron spectroscopy (XPS) (5700C Multitechnique System, Physical Electronics), using MgK_α radiation (h_m = 1253.6 eV). General spectra were recorded for the samples by scanning the binding energy (BE) from 0 to 1200 eV. The BE of the Pt 4f core level and full width at half maximum (FWHM) values were used to assess the chemical state of Pt. The chlorine content of the catalysts was also measured, considering BE values between 198-199 and 200-202 eV for inorganic and organic chorine, respectively. BE values were corrected for the effects of sample charging by taking the C1s peak (284.6 eV) as an internal standard. The data analysis procedure involved smoothing, a Shirley background subtraction, and curve fitting using mixed Gaussian-Lorentzian functions by a least-squares method. The atomic ratios of the elements were calculated from the relative peak areas of the respective core level lines using Wagner sensitivity factors. The reduction of the catalysts was carried out in a separate reactor prior to the XPS measurements.

Metal dispersion on the reduced and used catalysts was determined by CO chemisorption at room temperature (PulseChemiSorb 2705, Micromeritics). Several pulses of CO were introduced until saturation of the catalyst surface. The number of exposed platinum atoms (Pt_s) was calculated from the CO chemisorption data (CO_{ads}). The stoichiometry of the adsorption of CO on platinum atoms (Pt_s/CO_{ads}) was assumed to be 1 [17-21].

Transmission electron microscopy (TEM) of the samples was carried out using a JEOL JEM-2100F microscope operating at 200 kV. The apparatus had a point resolution of 0.25 nm and was equipped with a STEM unit with a bright field detector, and a CCD ORIUS SC1000 camera. The samples were previously dispersed in ethanol and dropped onto holey carbon-coated Cu grids. Particle size distributions were obtained by counting between 100 and 200 particles on each sample. From the size distribution, it was determined the average diameter: $d_n = \sum n_i d_i / \sum n_i$, where n_i is the number of particles with diameter d_i.

The crystaline structure of the catalysts was analyzed by X-ray diffraction (XRD) (X'Pert PRO Panalytical Diffractometer). The powdered samples were scanned using CuK_α monochromatic radiation (λ = 0.15406 nm) and a Ge mono filter. A scanning range of 2Θ = 20 – 75º and scan step size of 0.020º with 5 s collection time were used.

XRD, TEM, XPS, CO chemisorption and -196 ºC N_2 adsorption-desorption were performed with the catalysts after reduction under a continuous hydrogen flow of 50 $Ncm^3 \cdot min^{-1}$ at 300 ºC for 2 h and then cooled to room temperature under helium flow.

2.3. Catalytic activity experiments

The HDC experiments were conducted in a continuous flow reaction system described elsewhere [1], consisting in a quartz fixed bed micro-reactor coupled to a gas-chromatograph with a FID detector to analyze the reaction products. The chromatographic column was made of silica (Plot Fused Silica 60m x 0.53mm ID, Bruker).

The operation conditions in those HDC experiments were: Atmospheric pressure, a total gas flow rate of 100 $Ncm^3 \cdot min^{-1}$ and a total chloromethane (CM) inlet concentration of 1000 ppmv (TCM plus DCM). The catalysts weight, the reaction temperature and the H_2/CM molar ratio were adjusted to the desired values in each run. Space-times (τ) in the range of 0.04 - 1.73 $kg \cdot h \cdot mol^{-1}$, reaction temperatures of 100 – 250 ºC and H_2/CM molar ratio of 10 – 100 were tested. The catalysts were reduced in situ under continuous H_2 flow prior to the HDC experiments.

The behavior of the catalysts was evaluated in terms of CM conversion, DCM turnover frequency (TOF) and selectivity to the different reaction products. TOF is defined as the number of converted molecules of dichloromethane per molecule of accessible atoms of platinum and time.

The results on the characterization and the catalysts performance experiments were reproducible in more than 95%. At least two measurements were done for each experimental result reported.

3. Results and Discussion

3.1. Characterization of the catalysts

Table 1 summarizes the values of BET surface area, external surface area, micropore volume obtained by adsorption/desorption of nitrogen at -196 ºC of the fresh-reduced Pt/C catalysts, and bulk platinum content of the catalysts. In all cases, the metal content determined by ICP-

MS was lower than the nominal load (0.5-2.0 %) used for impregnation. All the Pt/C catalysts showed BET surface areas well above 800 m^2/g and external or non-microporous areas in the vicinity of 150 m^2/g, confirming the significant contribution of mesoporosity [22]. The decrease of total (BET) surface area upon Pt impregnation with respect to the AC support accounts no more than 10% at the most. This affects mainly to the microporous area suggesting partial blockage of the entrance of micropores, most probable the narrowest ones.

The Pt 4f region of the XPS spectra of all the catalysts showed a doublet corresponding to Pt $4f_{5/2}$ and Pt $4f_{7/2}$. As representative example, Fig. 1 depicts the deconvoluted spectrum of the catalyst with a 1% of Pt. The separation between the Pt $4f_{5/2}$ and Pt $4f_{7/2}$ peaks, due to spin orbital splitting, is a quantized value of 3.33 eV. The Pt $4f_{7/2}$ peak lying at around 72.0 eV can be attributed to Pt^0 (zero-valent Pt), while the Pt $4f_{7/2}$ peak located at around 73.4 eV is related to Pt^{n+} (electro-deficient Pt) [1, 23, 24]. The relative distribution of Pt species (Pt^0 and Pt^{n+}) on the surface of the catalysts, obtained by deconvolution of the XPS Pt 4f region, are summarized in

Table 2. As can be seen, Pt^0 is by far the predominant state in all the cases, must probably as a result of the reduction step included in the preparation procedure. The Pt^0/Pt^{n+} ratio increased with Pt loading, probably due to the lower ratio of surface oxygen groups to Pt (Pt^{n+} is formed upon interaction with those groups [25-28]). The chlorine content of the reduced catalysts was also calculated.

Table 2 shows the inorganic and organic chlorine contents of the reduced catalysts obtained from the deconvolution of the Cl_{2p} XPS spectra. The presence of chlorine on the surface of the catalysts is due to the platinum precursor ($H_2PtCl_6 \cdot 6H_2O$) used in its synthesis. The chlorine contents were similar in all the catalysts but it can be observed a slight decrease with the platinum content.

Table 3 collects the values of dispersion and average particle size of Pt of the fresh-reduced Pt/C catalysts. As can be seen, high dispersion values of the metallic phase were obtained in good agreement with the results reported for similar catalysts in previous works [15, 16]. The values of average particle size obtained by TEM measurements were lower than the obtained by CO chemisorption, being both fairly low. Fig. 2 shows TEM images of the Pt/C catalysts with 1% and 1.5% Pt loadings. Only the electrons scattered at very high angle contribute to form the image, and therefore, the signal intensity is strongly related to the atomic number of the element allowing to distinguish heavy elements like Pt from the light carbon atoms of the support. The large majority of the Pt particles show quasi-spherical shapes. The distributions of Pt particles size of the fresh-reduced 1% Pt/C and 1.5% Pt/C catalysts are depicted in Fig. 2. As can be seen, Pt particles with sizes between 1.0 and 4.0 nm were obtained, being most of the metallic particles within a narrow range of frankly small particles (1.5-2.0 nm).

The XRD patterns of the fresh-reduced Pt/C catalysts and the activated carbon support are presented in Figure 3. All the diffractograms showed the peak of the hexagonal carbon at 2ϴ around 26.6º and the other peaks of the carbon support around 40.8º and 50.0º. The peak associated with zero-valent platinum, located at a 2ϴ value of 40.0º [29] is not observed in the patterns of the catalysts, most probably due to the high dispersion of platinum on the surface, consistently with the results of

Table 3. However, peaks at 2ϴ value of 39.8º can be observed, which can be due to platinum oxides or other platinum compounds formed by interaction with surface oxygen groups of the AC.

3.2. Hydrodechlorination activity

3.2.1. Influence of Pt content

The catalysts were tested in the HDC of mixtures of DCM and TCM. Fig. 4 shows the evolution of DCM conversion in the HDC of an equimolar mixture of DCM and TCM (500 ppm_v each one) at 200 and 250 ºC, 1.2 kg·h·mol^{-1}space-time and H_2/CM molar ratio of 100. Complete conversion of TCM was maintained in all cases along the whole time on stream.

Table 4 presents the conversion values and selectivities (S = Product moles/Total moles · 100) to the major products (methane and MCM) at the end of the experiments (16 h on stream). As expected, the results showed a clear increase of DCM conversion with temperature and platinum content of the catalyst, being close to 100% with the 2.0% Pt/C at 250 ºC, while at 200 ºC less than 30% was achieved. Increasing the metal content of the catalyst, increases substantially the number of available active sites since higher metal contents are in this case accompanied by similar or even higher dispersion (see

Table 3). As can be observed in

Table 4, the selectivity to methane was higher than 96.0% in all the cases. At 250 ºC with the 2% Pt/C catalyst more than 98.0% overall dechlorination was achieved.

TOF was calculated from DCM conversion values at 200 ºC, H_2/CM molar ratio of 100 and 1.2 kg·h·mol^{-1} space-time for the HDC of the equimolar mixture of DCM and TCM, with a total feed concentration of 1000 ppm and a total flow of 100 Ncm^3/min. The mean metal particle size and dispersion values for the catalysts were obtained by TEM. As can be seen in Fig. 5, the TOF increases somewhat with the platinum content, which can be attributed to the higher proportion of zero-valent Pt (see

Table 2). In a previous study [15], Pt^0 sites were claimed as the main active centers for chloromethane and hydrogen adsorption in Pt/C catalysts. Zero-valent Pt has shown also to be more resistant to poisoning by the products than electro-deficient Pt [30]. In addition, the small amount of electro-deficient Pt and the high dispersion and homogeneous distribution of Pt inhibit the formation of hydrocarbons of more than one carbon atom that may promote coke deposition. In previous studies, it was found that formation of hydrocarbons higher than methane is favored by the reaction of two chlorinated radicals adsorbed on adjacent electro-deficient metallic sites [13-15].

3.2.2. Influence of mixture composition and operating conditions

The HDC of mixtures with different proportions of DCM and TCM was investigated. Fig. 6 shows dichloromethane and chloroform conversions and the selectivity to the main reaction product, methane, with the 1% Pt/C catalyst, as a function of the relative proportion of both reactants in feeding mixtures of 1000 ppm$_v$ total concentration. The overall dechlorination is also included. As in the previous experiments with equimolar mixtures, methane was by far the main reaction product (aprox. 95-98% selectivity), accompanied by low amounts of monochloromethane (S_{MCM} = 1.7-4.9%) and much lower of ethane (S_{C2H6} = 0.4-0.6%). The DCM conversion increased slightly and that of TCM decreased when increasing the DCM/TCM ratio beyond 2-3 in the inlet stream. This can be due to a competition between both compounds by the active centers of the catalyst [13]. However, the activity for both compounds was slightly lower than when working with each of them individually. In any case, the reactivity of chloroform is considerably higher than that of DCM as in the experiments before and therefore, increasing the DCM/TCM ratio leads to a significant decrease of the overall dechlorination.

Table 5 shows DCM and TCM initial conversions and methane selectivity in the HDC of equimolar mixtures (500 ppm_v each) using different H_2/CM molar ratios with the 2% Pt/C catalyst at 250 ºC and 1.2 $kg·h·mol^{-1}$ space time. TCM was completely converted at all the H_2/CM molar ratios tested (10-100). High DCM conversions were achieved even at the lowest H_2/CM molar ratio (83.5%), although that conversion increased somewhat with the H_2/CM ratio. The only reaction products were methane, ethane and MCM, being the selectivity to methane higher than 95% in all cases. No significant variations in selectivity were observed.

The effect of space-time in the HDC of the equimolar mixtures of DCM and TCM with the 2% Pt/C catalyst at 250 ºC and a H_2/CM ratio of 25 is shown in Fig. 7. Chloroform was completely converted even at the lowest space-time tested. On the other hand, DCM conversion showed a significant increase with increasing space-time up to around 0.8 $kg·h·mol^{-1}$ and beyond that value, no further significant increase was observed. This is consistent with previous results [13]. Hydrodechlorination of the mixture yielded mainly methane (S_{CH4} = 96.8-97.7%), and lower amounts of monochloromethane (S_{MCM} = 1.1-1.9%) and ethane (S_{C2H6} = 0.7-1.6%). The fact that the selectivity to methane was nearly 100% at very low space-time, indicates that, like in the case of the HDC of single chloromethanes, methane is a primary reaction product. Due to the high reactivity of TCM, and the high hydrogenolysis-hydrogenation ability of Pt/C catalysts [14], the reactions follow a parallel scheme with the total hydrodechlorination of the adsorbed radicals derived from TCM.

The effect of the reaction temperature on the TCM conversion in the HDC of the equimolar DCM/TCM mixtures was investigated, using the 0.5% Pt/C catalyst, at 0.4 $kg{\cdot}h{\cdot}mol^{-1}$ space-time, and a H_2/CM molar ratio of 10. The results are shown in Fig. 8, which includes also selectivities to the main reaction products (methane, ethane and MCM). TCM conversion undergoes a dramatic increase within the 125-200 ºC range. Nevertheless, DCM was practically unconverted at those conditions. Increasing the reaction temperature seems to increase the selectivity to methane although that effect occurs only at temperatures below 125 ºC, where fairly low TCM conversion was achieved.

4. Conclusions

Pt/C are very efficient catalysts for the hydrodechlorination of mixtures of dichloromethane and chloroform. In addition, the catalysts appear to be fairly stable. The catalyst with 2% of platinum allowed achieving complete TCM conversion and more than 90% for DCM with almost 98% selectivity to methane at 250 ºC, 1.2 $kg.h{\cdot}mol^{-1}$ space-time and a H_2/CM molar ratio of 100. Overall dechlorination above 98% was reached. Reducing the H_2/CM molar ratio up to 25 only a small decrease of DCM conversion was observed. Although some slight competition of both reactants for the active centers of the catalyst seems to occur, the activity for both compounds was close to that obtained with them individually. Unlike other results reported in the literature, the presence of different organochlorinated compounds cause scarce inhibition of their activity. The lower reactivity of DCM, at mild operating conditions, led to a decrease of overall dechlorination when increasing the proportion of DCM in the fed stream. The TOF values for DCM hydrodechlorination increases somewhat with the metal content, which can be attributed to the higher proportion of zero-valent species of platinum. The selectivity to reaction products suggests a parallel reactions scheme.

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TABLES:

Table 1. Metal content and characterization of the porous structure of the AC support and the fresh-reduced Pt/C catalysts

Catalyst	Platinum content (%)	S_{BET} (m^2/g)	S_{ext} (m^2/g)	Micropore volume (cm^3/g)
AC (*Merck*)	-	917	155	0.360
Pt/C (0.5%)	0.42	865	135	0.343
Pt/C (1%)	0.83	862	140	0.338
Pt/C (1.5%)	1.29	850	136	0.330
Pt/C (2%)	1.85	827	133	0.325

Table 2. Relative distribution of Pt species and chlorine content on the surface of the reduced catalysts

Catalyst	Pt^0 (%)	Pt^{n+} (%)	Pt^0/Pt^{n+}	% Cl_{2p}	% Cl_{inorg} (B.E. 198-199 eV)	% Cl_{org} (B.E. 200-202 eV)
Pt/C (0.5%)	66.6	33.4	2.0	0.12	13.1	86.9
Pt/C (1%)	70.3	29.7	2.4	0.07	18.7	81.4
Pt/C (1.5%)	73.4	26.6	2.8	0.04	18.6	81.4
Pt/C (2%)	82.4	17.6	4.7	0.05	14.9	85.1

Table 3. Metal dispersion (CO chemisorption) and average particle size values by CO chemisorption and TEM of the fresh-reduced Pt/C catalysts

Catalyst	**CO Chemisorption**		**TEM**		
	D (%)	Size (nm)	Size (nm)	SD (nm)	D (%)
Pt/C (0.5%)	32	3.6	2.0	0.53	56.6
Pt/C (1%)	37	3.1	1.6	0.37	70.8
Pt/C (1.5%)	47	2.4	1.7	0.98	66.6
Pt/C (2%)	49	2.3	1.7	0.47	66.6

Table 4. Conversion of DCM and TCM and selectivities to methane and MCM at the end of the experiments of Figure 5 (16 h on stream)

Temperature (ºC)	Catalyst	X_{DCM} (%)	X_{TCM} (%)	S_{CH4} (%)	S_{MCM} (%)
200	Pt/C (0.5%)	3.1	99.8	97.7	1.6
	Pt/C (1%)	7.9	100.0	97.6	1.9
	Pt/C (1.5%)	18.7	100.0	97.4	2.1
	Pt/C (2%)	29.0	100.0	96.0	2.9
250	Pt/C (0.5%)	41.6	100.0	96.6	2.4
	Pt/C (1%)	44.5	100.0	96.6	2.8
	Pt/C (1.5%)	58.1	100.0	96.7	2.9
	Pt/C (2%)	97.2	100.0	97.4	2.0

Table 5. Initial conversion of DCM and TCM and selectivity to methane in the HDC of equimolar mixtures (500 ppm_v each) with the 2% Pt/C catalyst at 250 °C, 1.2 $kg{\cdot}h{\cdot}mol^{-1}$ space-time and different H_2/CM molar ratios

H_2/CM	X_0 DCM (%)	X_0 TCM (%)	S_{CH4} (%)
10	83.5	100	95.7
25	87.8	100	97.0
50	89.6	100	97.2
100	91.6	100	96.9

FIGURES

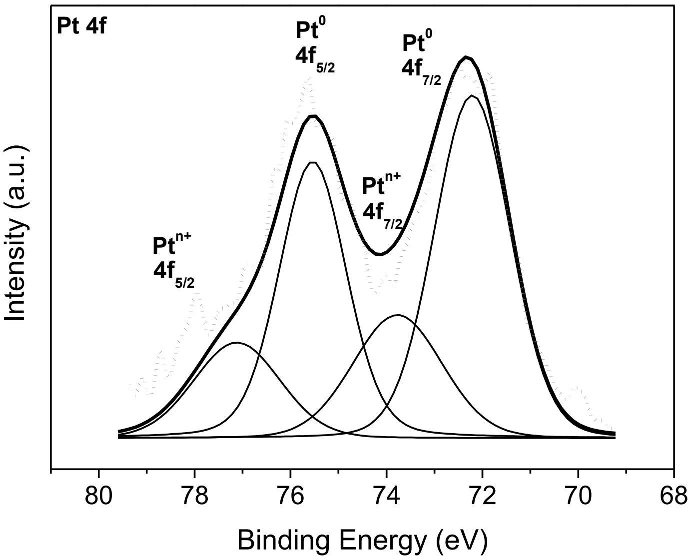

Figure 1. Deconvoluted Pt 4f spectra of Pt/C (1%) catalyst after reduction in H_2 at 300 ºC

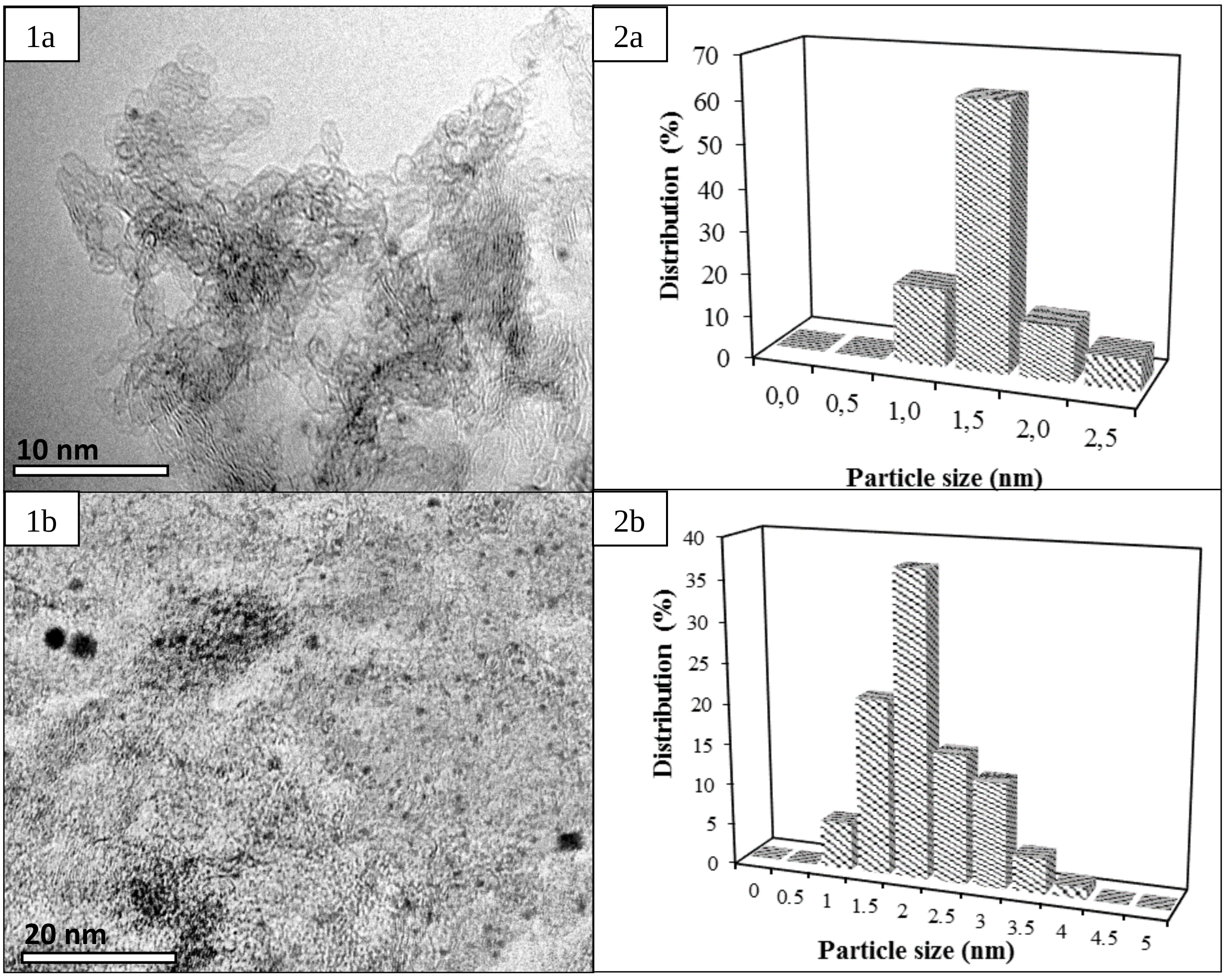

Figure 2. TEM image (1) and metal particle size distribution (2) of the fresh-reduced Pt/C (1%) (a) and Pt/C (1.5%) (b) catalysts

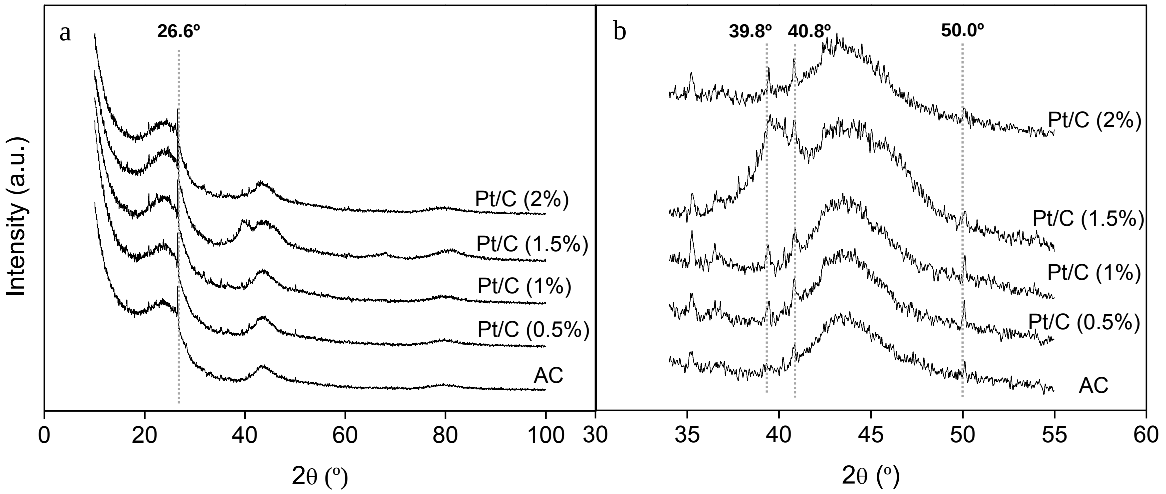

Figure 3. XRD patterns of the Pt/C catalysts and the support (a). Partial detail (b)

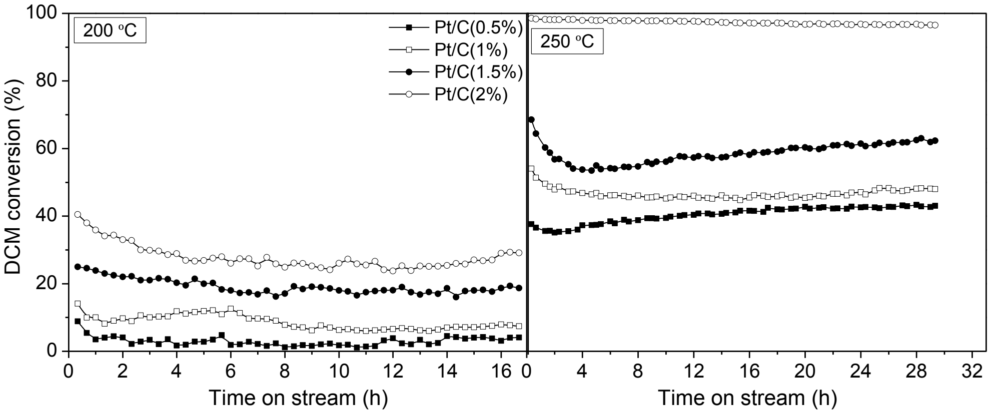

Figure 4. DCM conversion upon time on stream in the HDC of mixtures of DCM and TCM (500 ppm$_v$ each) at 200 and 250 ºC with the Pt/C catalysts (τ: 1.2 kg·h·mol^{-1}; H_2/CM molar ratio: 100)

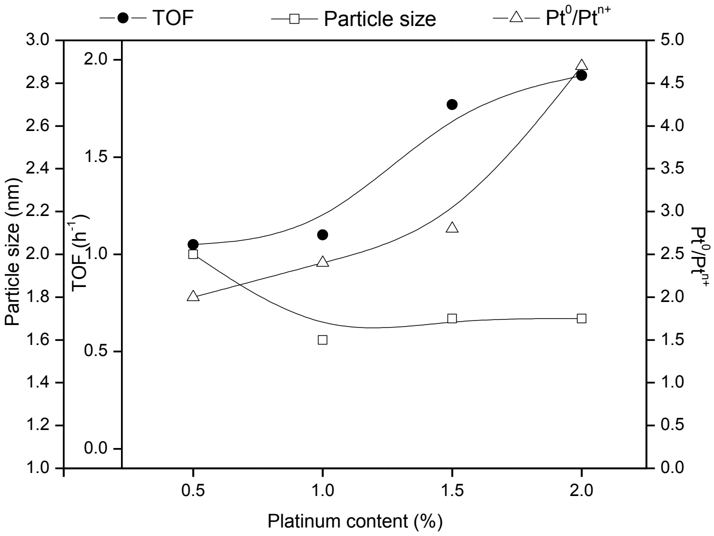

Figure 5. Values of turnover frequency (TOF), particle size and Pt^0/Pt^{n+} ratio for the Pt/C catalysts

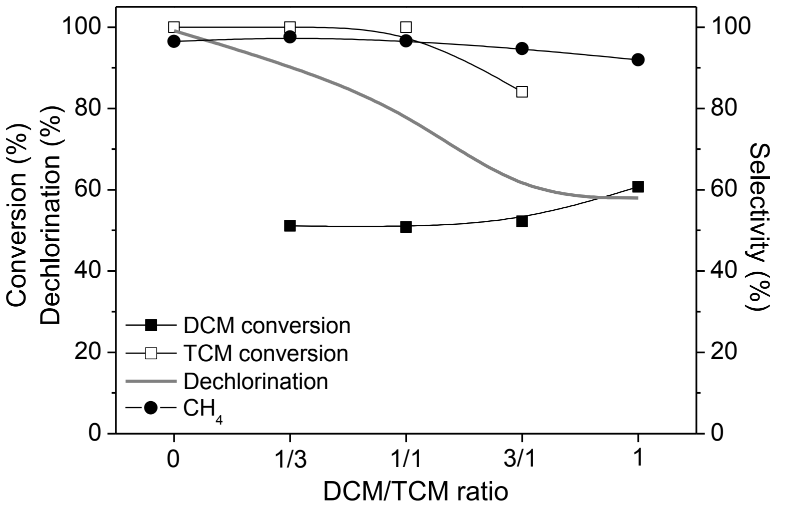

Figure 6. Conversion of DCM and TCM, selectivity to methane and overall dechlorination vs inlet concentrations at 250 °C, 1.2 kg·h·mol^{-1} space-time and H_2/CM molar ratio of 100 with the 1% Pt/C catalyst

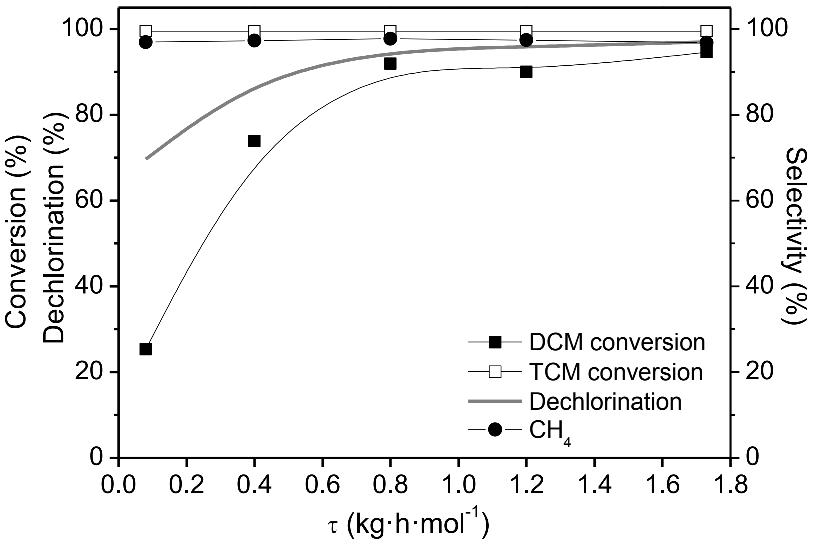

Figure 7. Conversion of DCM and TCM, selectivity to methane and overall dechlorination in the HDC of equimolar mixtures (500 ppm$_v$ each) with the 2% Pt/C catalyst at 250 °C, H_2/CM molar ratio of 25 and different space-times

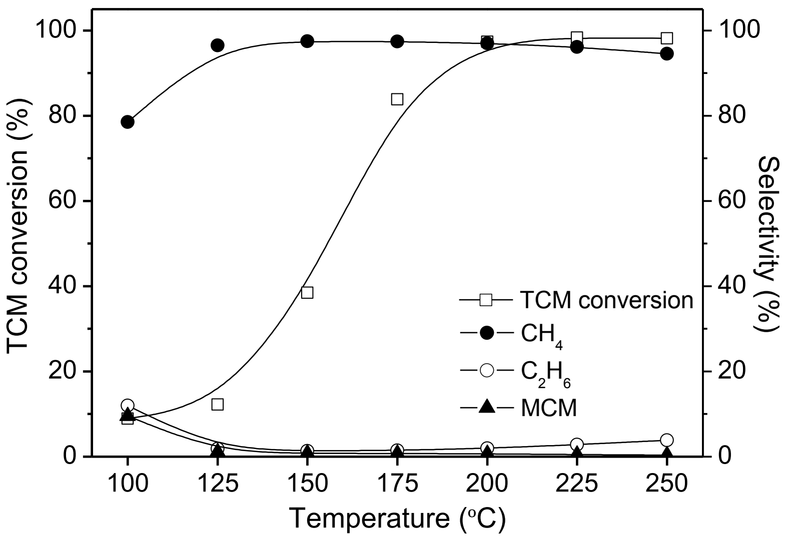

Figure 8. Effect of the reaction temperature on the conversion of TCM and selectivities to methane, ethane and MCM in the HDC of equimolar mixtures of DCM and TCM (500 ppm_v each) with the 0.5% Pt/C catalyst at 0.4 $kg \cdot h \cdot mol^{-1}$ space-time and H_2/CM molar ratio of 10