



# Kinetic study of the gas-phase hydrogenation of aromatic and aliphatic organochlorinated compounds using a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst

Elena López, Salvador Ordóñez\*, Herminio Sastre,  
Fernando V. Díez

*Department of Chemical and Environmental Engineering, University of Oviedo,  
Julián Clavería s/n, 33071 Oviedo, Spain*

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## Abstract

The hydrodechlorination of dichloromethane (DCM), tetrachloroethylene (TTCE), chlorobenzene (CBZ) and 1,2-dichlorobenzene (DCBZ), all of them alone and in mixtures, over a commercial Pd/Al<sub>2</sub>O<sub>3</sub> catalyst in a continuous packed-bed reactor was studied in the present work. Results indicate that the reaction kinetics for the single compounds are pseudo-first order kinetics. The reactivity of the compounds studied is very different. So, whereas aromatic compounds and tetrachloroethylene can be fully converted at the operation conditions reported in this work, dichloromethane conversions are lower than 30% in all the cases. The hydrodechlorination of mixtures of organochlorinated compounds shows important inhibition effects, these effects increase as the number of chlorine atoms in the molecule increase. Reaction kinetics for the hydrogenation of mixtures can be represented by a Langmuir–Hinshelwood model.

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*Keywords:* Dichloromethane; Tetrachloroethylene; Chlorobenzene; 1,2-Dichlorobenzene; Palladium/alumina catalyst; Catalytic hydrodechlorination; Inhibition effects; Langmuir–Hinshelwood model

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## 1. Introduction

Dichloromethane (DCM), tetrachloroethylene (TTCE), chlorobenzene (CBZ) and 1,2-dichlorobenzene (DCBZ) are widely used as solvents, extractants, dry-cleaners, degreasing agents, pesticides, etc., due to their physical and chemical properties (they are efficient

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\* Corresponding author. Tel.: +34-98-5103437; fax: +34-98-5103434.

E-mail address: salorga@correo.uniovi.es (S. Ordóñez).

solvents for greases and many organic compounds and most of them are not flammable). So, important amounts of residues containing these compounds are produced (they are among the organochlorinated compounds that are released into the atmosphere in the greatest quantities, according to EPA reports [1]), and constitute a very important environmental hazard due to their toxicity and carcinogenic character [2,3]. Moreover, these compounds contribute to global warming, and the formation of photochemical smog [2].

The conventional technique for the abatement of these wastes is thermal incineration, but this technique has important disadvantages. Chlorine is a flame inhibitor; hence high combustion temperatures are needed, which increases the cost of the process. Furthermore, very harmful partial oxidation by-products such as phosgene, dibenzofurans and dibenzodioxins can be released during thermal incineration [4].

Catalytic hydrodechlorination is an environmentally interesting alternative to thermal incineration [5]. This process consists of reacting the organochlorinated compounds with hydrogen, yielding hydrogen chloride and hydrocarbons. Hydrogen chloride can be easily separated by alkaline washing, whereas hydrocarbons can be burned or recovered. The process requires a catalyst in order to operate at mild temperatures.

Precious metals (Pd, Pt and Rh) [6,7] and hydro-treatment catalysts (Ni-Mo) [7,8] have shown activity for hydrodechlorination reactions. The most active hydrodechlorination catalysts are supported precious metals, active at moderate pressure and temperature (1–0.5 MPa, 250 °C), whereas hydro-treatment catalysts operate at more severe conditions (10 MPa,  $T > 350$  °C). Most studies on hydrodechlorination have been carried out using precious metal catalysts: Rh/SiO<sub>2</sub> was used by Bozelli et al. [9] for 1,2-dichloroethane and trichloroethylene; Pt on alumina was used by Kim et al. [10] for carbon tetrachloride, by Noelke and Rase [11] for chloroform and by Weiss and Krieger [6] for vinyl chloride and dichloroethylenes.

Palladium-based catalysts have been studied by several authors for the hydrodechlorination of chlorobenzene [12], difluorodichloromethane [13,14], 1,1,2-trichlorotrifluoroethane [15] and 1,2-dichloroethane [16]. However, in most of these works, hydrodechlorination reactions were carried out with pure halogenated/H<sub>2</sub> systems, not useful for environmental purposes.

In the previous studies of our group, it has been observed that supported palladium catalysts show high activity and stability for the hydrodechlorination of chloro-aliphatic compounds, such as TTCE, trichloroethylene and dichloroethylene [17]. Several supports have been tested, alumina being the support that leads to the most active and stable catalysts [18]. The influence of process parameters (temperature, pressure, hydrogen flow and nature of solvent) on both activity and stability of this catalyst has been studied: it was found that higher temperature leads to higher initial activity but faster deactivation; increasing hydrogen flow rates produces higher activity and stability of the catalyst, whereas pressure and solvent have no significant effect [19].

The main aim of this work is to study the kinetics of the hydrodechlorination of DCM, TTCE, CBZ and DCBZ, both alone and in mixtures, in an organic matrix, over a commercial palladium catalyst. These studies are of practical relevance, as organochlorinated compounds are often present in liquid wastes dissolved in an organic matrix, as solids that must be dissolved for catalytic processing, or in mixtures. Besides this, it would be more advantageous from an economic point of view to be able to feed mixtures to the hydrodechlorination process rather than pure compounds. Most studies on hydrodechlorination reactions in the

presence of organic solvent have been devoted to hydro-treatment catalysts [8,20], the studies using palladium being scarce [19,21,22]. Hagh and Allen [23] have carried out a study comparing Pd and hydro-treatment catalysts for the hydrodechlorination of chloro- and dichloro-benzene. The main finding was that the activity of both the catalysts is similar, but in the case of dichlorobenzene, selectivity for chlorobenzene was higher for the Pd catalyst than for hydro-treatment catalysts. On the other hand, to the best of our knowledge, there are no works published dealing with mixture effects when different organochlorinated compounds are processed together, even though inhibition effects are important in similar processes such as hydro-treating of oil and coal fractions [24]. In the previous works of our group, it has been considered the hydrodechlorination of mixtures containing dichloroethylene, trichloroethylene and tetrachloroethylene [25]. However, it is also important to consider the hydrodechlorination of mixtures containing both aliphatic and aromatic compounds, in spite of these organochlorinated compounds are often present in industrial wastes.

## 2. Experimental

### 2.1. Materials

The chemicals used in this work (DCM, TTCE, CBZ, DCBZ, TCE, benzene, toluene, methylcyclohexane and decahydronaphtalene) were supplied by Panreac, Fluka and Merck, with a minimum purity of 98%. Hydrogen was supplied by Air Products with a minimum purity of 99.999% and  $\alpha$ -alumina was supplied by Acros. The catalyst tested was Engelhard Escat 16, a commercial palladium supported on alumina catalyst, whose composition and textural characteristics are given in Table 1. The catalyst is available as pellets, which were crushed and sieved to a particle size between 0.1 and 0.355 mm.

### 2.2. Reaction studies: equipment and experimental procedure

Reactions were carried out in a fixed-bed reactor consisting of a 9 mm i.d., 450 mm length stainless steel cylinder, placed inside a tubular electric furnace and equipped with five thermocouples at different reactor heights for monitoring temperature. The reactor contained between 0.25 and 1 g of catalyst mixed with alumina, placed in the mid-section of the reactor. The bottom and top sections were packed with  $\alpha$ -alumina, the upper alumina-bed being used as the pre-heating zone. The catalyst was activated in situ before use by passing through the reactor 0.90 Nl/min of hydrogen at 350 °C and 0.5 MPa for 6 h. The liquid feed flowed downwards through the reactor, pumped by a Kontron T-414 liquid chromatography pump. At reaction conditions, all liquid feeds were completely vaporised. Hydrogen was fed

Table 1  
Composition and textural characteristics of Engelhard Escat 16 catalyst

Composition (wt.%)	0.5% Pd/Al <sub>2</sub> O <sub>3</sub>
BET specific surface (m <sup>2</sup> /g)	92.25
BJH desorption pore volume (cm <sup>3</sup> /g)	0.46
Average pore diameter (nm)	18.22

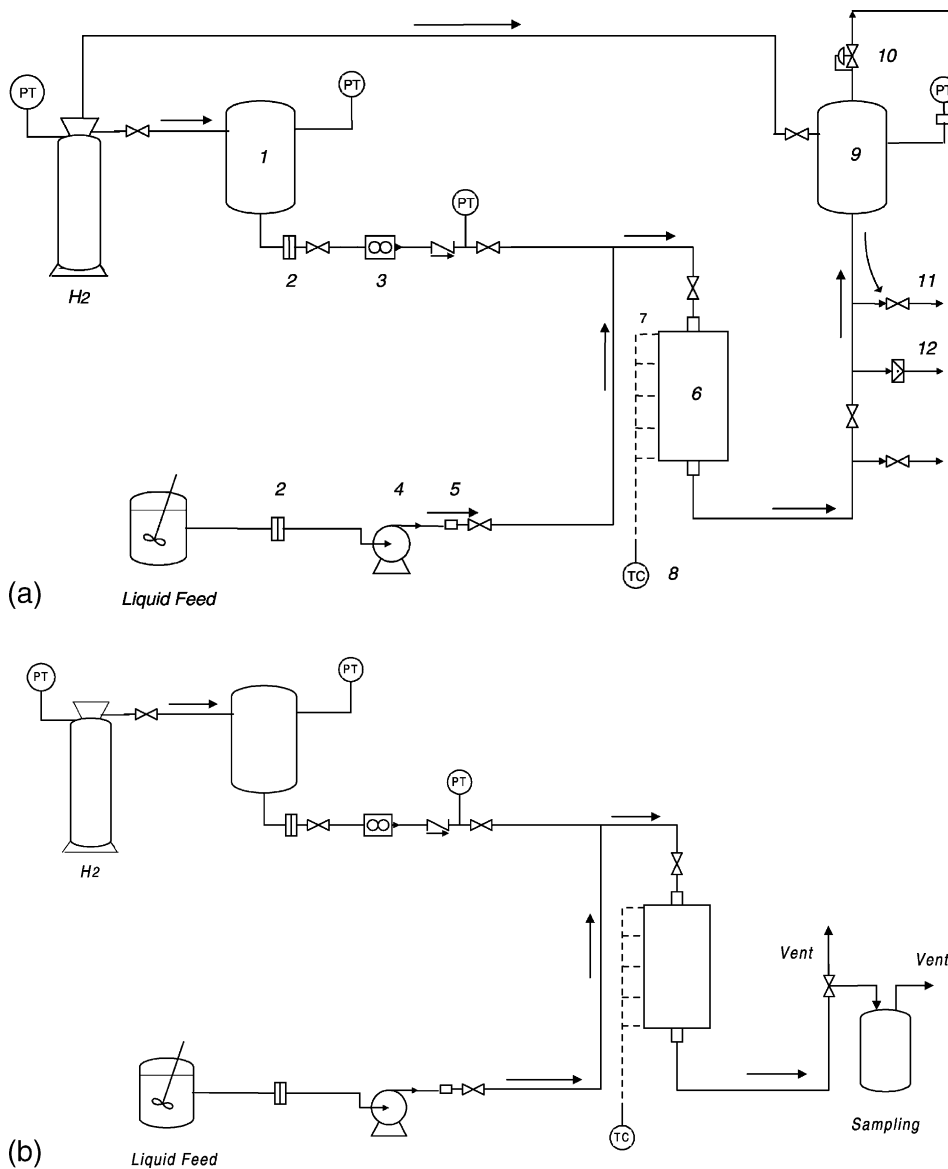


Fig. 1. (a) Scheme of the hydrodechlorination reactor for the experiments carried out at 5 bar: (1) hydrogen cylinder, (2) filter, (3) mass-flow regulator, (4) liquid pump, (5) pulse damper, (6) reactor, (7) thermocouples, (8) temperature controller, (9) receiver, (10) back-pressure regulator, (11) sampling, (12) rupture disk. (b) Scheme of the hydrodechlorination reactor for the experiments carried out at atmospheric pressure.

co-currently, the flow rate being controlled by a Brooks 5850 TR/X mass-flow regulator. The reaction products were collected in a stainless steel Teflon-lined cylindrical receiver. The top of the receiver was connected to a Tescom 26-1723-24 back-pressure regulator which maintained the operating pressure (0.5 MPa) by venting the excess gas. Liquid samples were taken by emptying the receiver at selected time intervals. All the elements were constructed of Hastelloy-C, which is resistant to the corrosion caused by the hydrogen chloride released during the reaction. When DCM was fed to the reactor, in order to collect chloromethanes more efficiently, the stainless steel receiver was substituted by a glass receiver immersed in liquid nitrogen where all organic reactants and reaction products are condensed. So, experiments were carried out at atmospheric pressure instead of 0.5 MPa, although this variation does not have any influence on the results. The other parts of the set-up were kept as in the initial set-up. The set-up, whose schematic diagram is as shown in Fig. 1a and b, was fitted with safety features such as temperature and pressure controls, and a rupture disk. An initial operational period of 4 h was allowed to permit the catalyst to reach constant activity before taking representative samples. To avoid transient effects, the samples taken after changing the operational conditions were discarded.

### 2.3. Analysis

Reaction products were analysed by gas chromatography in a Hewlett-Packard 5890A apparatus equipped with a FID detector, using decahydronaphthalene as internal standard and a HP-1 30 m capillary column. The oven was kept at 60 °C for an initial period of 15 min and then heated to 180 °C at 6 °C/min. Peak assignment was performed by GC–mass spectra (Hewlett-Packard 5987A), and responses were determined using standard calibration mixtures.

## 3. Results and discussion

### 3.1. Preliminary experiment

A preliminary experiment was carried out to check the extension of the reaction without catalyst (the reactor filled only with alumina). Conditions were 1 MPa, 350 °C, reactor feed 0.7 ml/min of 10 wt.% CBZ dissolved in toluene, and hydrogen flow rate 21.4 times the stoichiometric amount considering that all CBZ reacts yielding benzene. Under these conditions, the most severe used in the experiments, CBZ conversion was below 1.1%. In the previous works, negligible DCM and TTCE conversions were obtained in the absence of catalyst at these conditions [7].

### 3.2. Kinetic studies of the hydrodechlorination of single compounds: DCM, TTCE, CBZ and DCBZ

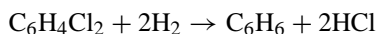
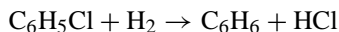
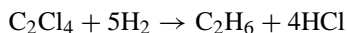
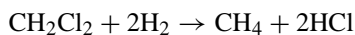
In these experiments, the liquid mixtures fed to the reactor consisted of 10 wt.% solutions of one organochlorinated compound (DCM, TTCE, CBZ or DCBZ) in toluene. A hydrogen excess 10:1 over the stoichiometric amount was used considering the reaction of DCM to

methane, TTCE to ethane, and CBZ and DCBZ to benzene; these products being detected by gas-chromatography as the only non-chlorinated reaction products. In the calculations, it is also considered reaction of 5% of toluene to methyl-cyclohexane. As mentioned in Section 2, TTCE, CBZ and DCBZ experiments were carried out at 0.5 MPa pressure, whereas in the case of DCM, the experiments were carried out at 0.1 MPa. In the previous works of our group, a negligible influence of the operation pressure in this range was demonstrated [17]. Operation temperature was fixed in the range of 150–325 °C in order to both make sure that all reactants were present in the reactor as gases, and ensure the stability of the catalyst during the experiments (higher temperatures lead to fast catalyst deactivation). Space times between 0 and 3 min g of catalyst/mmol of reactant were reached by varying the flow rate of the liquid feed in the range of 0.4–2.5 ml/min and the amount of catalyst in the range of 0.25–0.5 g, keeping constant the H<sub>2</sub>:organochlorinated compound ratio. The highest temperature and space time were used in the case of DCM, as it was found to be the less reactive among the compounds studied. In the previous experiments, it was demonstrated that nature of the solvent (aliphatic or aromatic) does not influence noticeably on the catalyst activity [19].

In all the experiments, the reaction products were hydrogen chloride and hydrocarbons (methane from DCM, ethane from TTCE and benzene from CBZ and DCBZ). In the case of TTCE and DCBZ, very small amounts of organochlorinated by-products were detected (trichloroethylene and chlorobenzene, respectively), but selectivities toward total hydrodechlorination were always higher than 95%. The solvent did not react in appreciable extension (conversion < 1%), only small amounts of methyl-cyclohexane being observed. In the case of CBZ, conversions have been calculated considering both loss of reactants and formation of products, closing mass balances with an error lower than 2%. DCM and TTCE conversions were calculated from the concentration of reactants, since methane and ethane are permanent gases and its analysis is inaccurate.

In order to ensure the absence of organic compounds in the vapour phases (in the case of experiments carried out at 0.5 MPa), gas samples from the venting were collected using a glass receiver immersed in a liquid nitrogen flask. These samples were analysed by GC-FID and GC-MS. These analyses demonstrate that there are no light organics (as chloromethane or vinyl chloride), the concentration of the other organics (solvent, reactants and reaction products) corresponding to their vapour pressures and their influence in the calculations being negligible.

The reactions taking place are:



Experimental results obtained for the different organochlorinated compounds are as shown in Figs. 2–5.

Assuming that the reactor presents a PFR-like behaviour, pseudo-first order kinetics for all reactions and Arrhenius dependence of the kinetic constant with temperature, the

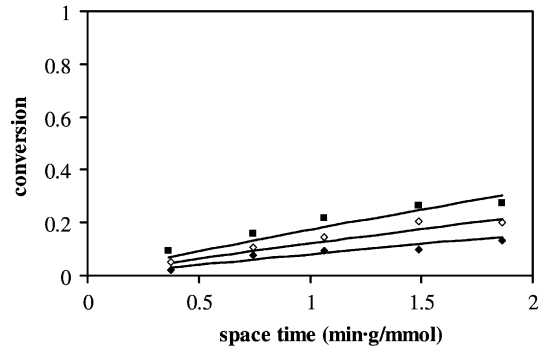


Fig. 2. Evolution of experimental (points) and predicted (line) conversion with space time for hydrodechlorination of dichloromethane at different temperatures: (◆) 250 °C, (◇) 275 °C, (■) 300 °C.

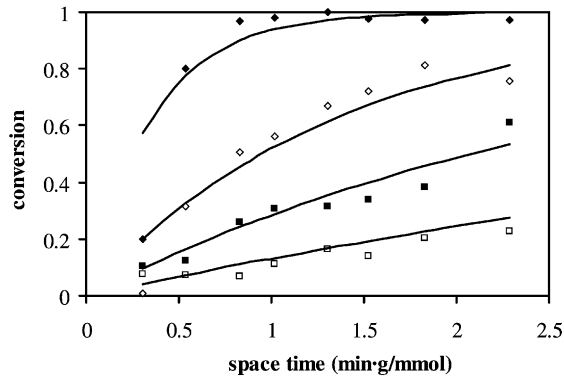


Fig. 3. Evolution of experimental (points) and predicted (line) conversion with space time for hydrodechlorination of tetrachloroethylene at different temperatures: (◆) 250 °C, (◇) 200 °C, (■) 175 °C, (□) 150 °C.

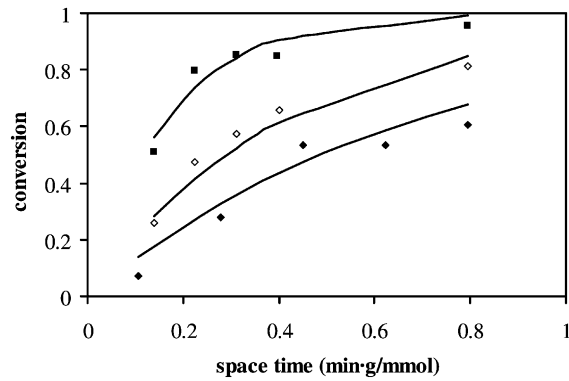


Fig. 4. Evolution of experimental (points) and predicted (line) conversion with space time for hydrodechlorination of chlorobenzene at different temperatures: (◆) 250 °C, (◇) 275 °C, (■) 325 °C.

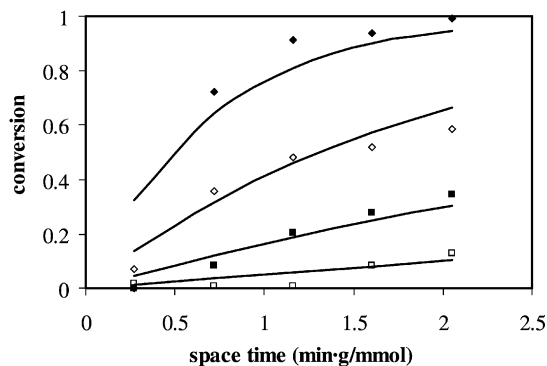


Fig. 5. Evolution of experimental (points) and predicted (line) conversion with space time for hydrodechlorination of *o*-dichlorobenzene at different temperatures: (◆) 250 °C, (◇) 225 °C, (■) 200 °C, (□) 175 °C.

predicted conversion (lines as shown in Figs. 2–5) and the parameters given in Table 2 are obtained. The kinetic parameters were calculated by fitting the resultant expressions to the experimental data. This was made by means of the non-linear least squares minimisation of the error in the prediction of conversions, using a simplex algorithm followed by a Powell minimisation algorithm. These mathematical tools are implemented in the commercial programme Scientist. The quality of the fit is quantified using the correlation coefficient ( $r$ ).

It is possible to consider a PFR-like behaviour when the by-pass effects and the axial dispersion effects are negligible; for it, it is necessary that (reactor diameter/particle diameter) > 10 and (catalytic bed length/particle diameter) > 50 [24,26]. In our case, the values are 18 and 100, respectively, so it is possible to assume this type of behaviour.

The absence of mass transfer limitations was theoretically demonstrated according to the procedure proposed [25] by Anderson and Boudart [27]. So, the dimensionless Damköhler number ( $Da$ , which express the ratio between the reaction on the mass transfer rates) is  $4.7 \times 10^{-7}$ , whereas the dimensionless Wheeler–Weisz number is  $1.3 \times 10^{-1}$ . These values indicate that both internal and external mass transfer limitations are not significant in our case. Thermal effects are also considered negligible when  $Da < 0.2$ .

In addition, further experiments have been carried out working with different catalysts weights (0.2–0.5 g) at constant space time (modifying liquid flow rates), and working with different particle diameters (0.05–0.25, 0.1–0.35, and 0.25–0.5 mm), obtaining in all the

Table 2

Activation energy ( $E_A$ ), kinetic constant at 250 °C ( $k$ ), and correlation coefficient ( $r$ ) for the hydrodechlorination reactions of DCM, TTCE, CBZ and DCBZ (single compounds)

	$E_A$ (kJ/mol)	$k$ (mmol/(min g MPa))	$r$
DCM	41.1	24	0.931
TTCE	55.1	366	0.976
CBZ	49.4	156	0.988
DCBZ	86.1	184	0.975



cases identical values of tetrachloroethylene conversions at 250 °C. These results ensure the absence of mass transfer limitations (external and internal, respectively).

Both the experimental results as shown in Figs. 2–5 and kinetic parameters in Table 2 indicate that the order of reactivity of the organochlorinated compounds studied is TTCE > DCBZ  $\cong$  CBZ  $\gg$  DCM. Most of the activation energies obtained in our experiments using a Pd commercial catalyst are lower than the ones reported in the literature. However, it is important to remark that most of these reported values are referred to hydro-treatment catalysts, which are less active than Pd catalysts [7]. The activation energy obtained in the previous works for hydrodechlorination of TTCE is 17–50 kJ/mol [8,20] using hydro-treatment catalysts. In the case of CBZ, Coq et al. [13] have obtained values of 80–125 kJ/mol using Pd, Rh and Pd-Rh catalysts, whereas Meyer et al. [22] and Converti et al. [21] gave values of 175.3 kJ/mol for hydrodechlorination of CBZ and 146.4 for hydrodechlorination of DCBZ, but using hydro-treatment catalysts. For hydrodechlorination of DCM over hydro-treatment catalysts, Converti et al. [21] and Meyer et al. [22], have obtained a value of 237.6 kJ/mol.

At the conditions studied, very high conversion can be attained for all the compounds, except for DCM, for which a maximum conversion of 28% is attained at 300 °C and 1.5 min g/mmol. In the case of CBZ and DCBZ, process continues to completion yielding simple benzene (BZ) as the final product, in a reaction sequence DCBZ  $\rightarrow$  CBZ  $\rightarrow$  BZ. Removal of the first chlorine atom from DCBZ results in the same intermediate product, CBZ, but it is detected in a quantity <10%. Balko et al. [28] has also found a similar reactivity between CBZ and DCBZ [26].

### 3.3. Kinetic study of the hydrodechlorination of TTCE–CBZ mixtures

Two series of experiments with TTCE–CBZ mixtures were carried out at 250 °C and 0.5 MPa, feeding the reactor with liquid TTCE–CBZ solutions in toluene in the range of 0–1 mol/l. The feeds in the first series were 10 wt.% CBZ and CBZ:TTCE molar ratios of 1:1, 1:0.5, 1:0.25 and 1:0, and in the second series 10 wt.% TTCE and TTCE:CBZ molar ratios of 1:1, 1:0.5, 1:0.25 and 1:0. Space times of 0–7 min g of catalyst/mmol of TTCE and 0–10 min g of catalyst/mmol of CBZ were reached, by varying both the feed composition, and the flow rate of the liquid feed (0.4–3 ml/min), and the amount of catalyst (0.25–0.5 g). The H<sub>2</sub>:organochlorinated compounds molar ratio was maintained constant, resulting an excess of 10:1 over the stoichiometric amount (estimated as it was explained in Section 3.2).

Important mixture effects were observed when the two organochlorinated compounds were reacted together: CBZ conversion is drastically reduced in the presence of TTCE (Fig. 6), whereas the effect of CBZ on the hydrodechlorination of TTCE is smaller (Fig. 7).

This result can be explained assuming that the influence of the number of chlorine atoms attached to the organic structure on the adsorption strength and, hence in the inhibitory effect, is more marked than the effect of the type of organic structure (TTCE has four chlorine atoms and CBZ only one, whereas aromatic structures are considered to hold stronger interaction with the metallic surface). The important role of the chlorine atoms attached to the organic structure in metal-catalysed hydrodechlorination reactions and their substantial role in the adsorption have been stated by other authors [6,24]. This hypothesis is also consistent with the observed negligible effect of the solvent on the catalyst performance,

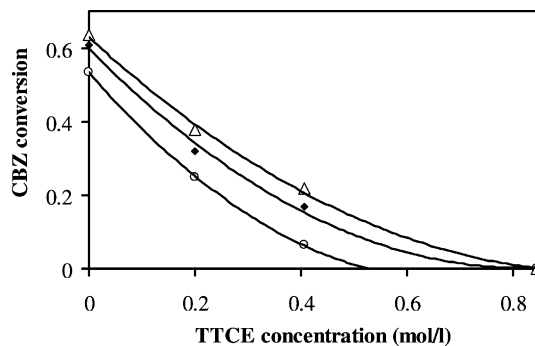


Fig. 6. Influence of inlet TTCE concentration on CBZ conversion (0.8 mol/l CBZ). Space time: (○) 0.6, (◆) 0.8 and (△) 1 min g/mmol.

and with the higher reactivity of TTCE in comparison with CBZ observed in this work for the hydrodechlorination of single compounds.

When mixture effects on the kinetics of hydrogenolysis or hydrogenation reactions are considered, the most successful models are those based on Langmuir–Hinshelwood (LH) mechanisms [22,25]. Considering the high affinity of hydrogen for the Pd surface, the chemisorption of hydrogen is usually considered as dissociative. With respect to the adsorption of the organochlorinated compound, two possibilities can be considered: chemisorption on the same active sites than hydrogen, or chemisorption of hydrogen and organochlorinated compounds on different active sites. The resulting models are usually named Langmuir–Hinshelwood over analogous sites (LHA) and Langmuir–Hinshelwood over non-analogous sites (LHNA), respectively. Taking into account that hydrogen is present in large excess and, hence its partial pressure is almost constant in all the experiments (0.43 MPa), the kinetic equation derived for both the cases can be written as:

$$(-r_i) = \frac{j'_i p_i}{(1 + K'_i p_i + K'_j p_j)^n} \quad (1)$$

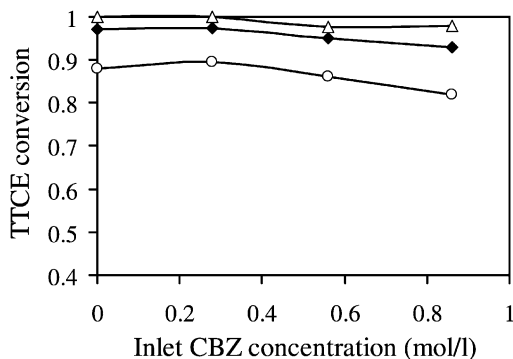


Fig. 7. Influence of inlet CBZ concentration on TTCE conversion (0.5 mol/l TTCE). Space time: (○) 0.6, (◆) 0.8 and (△) 1 min g/mmol.

Table 3  
Summary of the rate models with estimated parameters and correlation coefficients

Model	$j'_i$ (mmol/(min g MPa))	$K'_i$ (MPa <sup>-1</sup> )	$r$
LHA	$j'_i = \frac{j_i K_i K_H^{1/2} p_H^{1/2}}{(1 + K_H^{1/2} p_H^{1/2})^2}$	$K'_i = \frac{K_i}{(1 + K_H^{1/2} p_H^{1/2})}$	0.994
	TTCE	$6.284 \times 10^2$	
	CBZ	$2.678 \times 10^2$	
LHNA	$j'_i = \frac{j_i K_i K_H^{1/2} p_H^{1/2}}{(1 + K_H^{1/2} p_H^{1/2})}$	$K'_i = K_i$	0.985
	TTCE	$1.800 \times 10^7$	
	CBZ	$4.207 \times 10^5$	

where exponent  $n$  is equal to 1 for LHNA model and equal to 2 for LHA model,  $p_i$  represents partial pressure of component  $i$ ,  $j_i$  is the intrinsic kinetic constant and  $K_i$  the adsorption constant for component  $i$ . The constants  $j'_i$  and  $K'_i$  are defined in Table 3 for both the models.

The kinetic parameters for the two models were calculated by fitting the two rate expressions corresponding to Eq. (1) to the experimental data. The computational procedure was mentioned in the previously mentioned section, but using the EPISODE package to integrate the differential equations system (ODE). This mathematical tool is also implemented in the commercial programme Scientist.

Results (Table 3) show that although both the models fit fairly well in the experimental data, LHA model presents the best correlation coefficient, in addition to provide meaningful adsorption constants. So, the values of the kinetic and adsorption constants for the tetrachloroethylene are in the same order of magnitude in this work and in the other studies carried out at similar conditions but working with tetrachloroethylene–trichloroethylene–dichloroethylene mixtures [22,25].

Experimental and predicted values (LHA model) are compared as shown in Fig. 8 for all the experimental points. It can be observed that the fit for the proposed model is fairly good. The tendency of the values of the constants is in good agreement with the experimental observations: TTCE is more reactive and presents higher inhibition capacity than CBZ.

In conclusion, it has been demonstrated that pseudo-first order kinetics fits the hydrodechlorination of the single organochlorinated compounds with reasonable accuracy. However, the inhibition effects observed in the hydrodechlorination of TTCE–CBZ mixtures cannot be represented by this model, good results being obtained by a LHA model. LHA model can also represent properly the behaviour observed for single compounds.

### 3.4. Study of the influence of DCM on the hydrodechlorination of TTCE and CBZ

The next series of experiments were devoted to study the influence of the presence of DCM on the hydrodechlorination of TTCE and CBZ. Experiments were carried out at 0.1 MPa and 250 °C. The liquid reaction feed contained, for the first series of experiments (DCM–CBZ dissolved in toluene), 10 wt.% DCM and DCM:CBZ molar ratios of 1:1, 1:0.5, 1:0.25 and 1:0, and for the second series (DCM–TTCE dissolved in toluene), 10 wt.% DCM

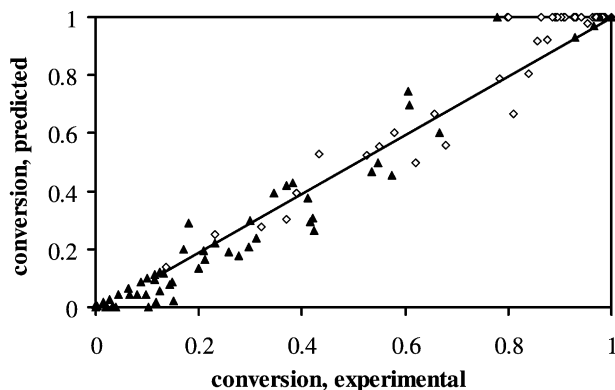


Fig. 8. Parity plot comparing the experimentally measured conversion of ( $\blacktriangle$ ) CBZ and ( $\diamond$ ) TTCE with the prediction of LHA model.

and DCM:TTCE molar ratios of 1:1, 1:0.5, 1:0.25, and 1:0. In an additional experiment, the hydrodechlorination of the mixture with a 5 wt.% CBZ, CBZ:DCM and CBZ:TTCE molar ratios of 1:1:1, dissolved in toluene was studied. A hydrogen excess of 10:1 over the stoichiometric required was fed to the reactor in all the experiments. Space times of 0–5 min g of catalyst/mmol CBZ (DCM–CBZ mixtures), 0–3 min g/mmol TTCE (DCM–TTCE mixtures) and 0.1–1.3 min g/ml of liquid feed (ternary mixture) were reached changing the flow rate (0.4–3.7 ml/min) and concentrations of liquid feed. In all the experiments, 0.5 g of catalyst were charged to the reactor. Results for DCM, CBZ, or TTCE binary mixtures are represented as shown in Figs. 9 and 10, whereas conversions for the DCM–TTCE–CBZ ternary mixture compared with results for the single compounds are represented as shown in Fig. 11.

The order of reactivity observed is TTCE > CBZ > DCM, as in experiments on hydrodechlorination of single compounds. DCM inhibits strongly the hydrodechlorination of CBZ (Fig. 9), whereas no effect is observed in the hydrodechlorination of TTCE (Fig. 10).

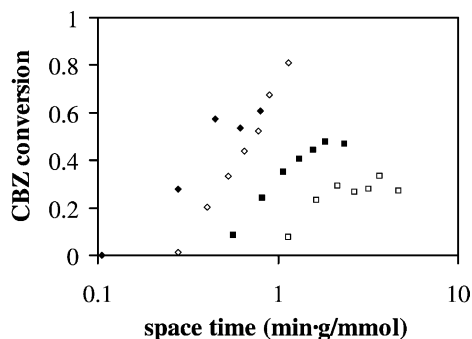


Fig. 9. Evolution of chlorobenzene conversion with space time for hydrodechlorination of chlorobenzene at the following DCM:CBZ molar ratios: ( $\blacklozenge$ ) 0, ( $\diamond$ ) 1, ( $\blacksquare$ ) 2, ( $\square$ ) 4.

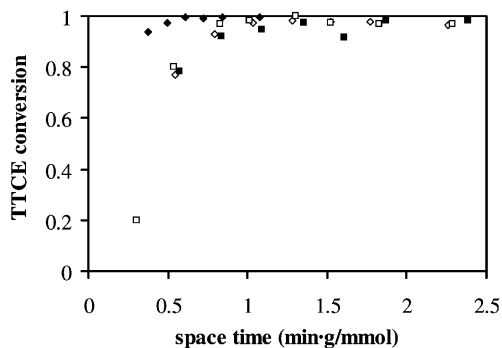


Fig. 10. Evolution of tetrachloroethylene conversion with space time for hydrodechlorination of tetrachloroethylene at the following DCM:TTCE molar ratios: (◆) 0, (◇) 1, (■) 2, (□) 4.

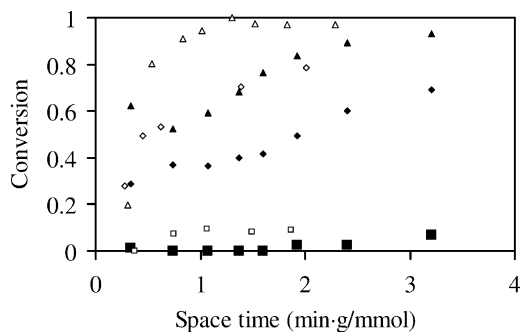


Fig. 11. Evolution of conversion with space time for hydrodechlorination of the following organochlorinated compounds: dichloromethane, (□) alone and (■) in the ternary mixture; tetrachloroethylene, (△) alone, (▲) in the ternary mixture; chlorobenzene, (◇) alone, (◆) in the ternary mixture. Reaction conditions: 250 °C and 0.5 MPa.

These results can be explained assuming that the compounds with a higher number of chlorine atoms have stronger adsorption strength and a higher inhibition effect. Only in the case of the reaction of the ternary mixture, a decrease of TTCE conversion is observed (Fig. 11), due to a higher charge of chlorine atoms fed with TTCE.

#### 4. Conclusions

The hydrodechlorination of DCM, TTCE, CBZ and DCBZ over a Pd/Al<sub>2</sub>O<sub>3</sub> catalyst produced hydrocarbons (methane, ethane, and benzene) that can be safely recovered or burned, with selectivities higher than 95%. This result is very important, since the final aim of this work is the development of a clean technology for the treatment of organochlorinated compounds.

The kinetics of the hydrodechlorination of single organochlorinated compounds can be

fitted to a pseudo-first order equation with a reasonable accuracy. For TTCE–CBZ mixtures, inhibition effects are observed and best results are provided by a Langmuir–Hinshelwood model considering the adsorption of organochlorinated compounds and hydrogen over the same active sites. The order of reactivity is TTCE > CBZ > DCM, whereas the higher inhibition effect is shown by the compounds with a higher number of chlorine atoms.

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