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Inhibition effects of organosulphur compounds on the hydrodechlorination of tetrachloroethylene over Pd/Al_2O_3 catalysts

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Abstract

The hydrodechlorination of tetrachloroethylene in presence of thiophene over a commercial Pd/Al_2O_3 catalyst was studied in a continuous packed-bed reactor at different temperatures (200–300 °C) and thiophene concentrations (0–5 wt.%). Results indicate that thiophene reversibly decreases tetrachloroethylene conversion and increases the selectivity for trichloroethylene formation. The kinetics of the hydrodechlorination of tetrachloroethylene in the presence of thiophene to form trichloroethylene and ethane can be represented by a Langmuir–Hinshelwood model.

Keywords: Tetrachloroethylene; Thiophene; Palladium/alumina catalyst; Catalytic hydrodechlorination; Inhibition effects; Langmuir–Hinshelwood kinetics

1. Introduction

Tetrachloroethylene (TTCE) is an organochlorinated compound widely used as solvent in the chemical industry, as dry-cleaner, in the preparation of textile fibbers and as degreasing agent. So, important amounts of organic wastes containing this compound are produced and released to the environment (it is among the organochlorinated compounds that are released into the atmosphere in the greatest quantities, according to EPA reports [1]), producing a very important environmental hazard due to their toxicity and carcinogenic character [2,3].

The conventional technique for the abatement of these wastes is thermal incineration, but this technique has important disadvantages, such as the possibility of formation of very toxic partial oxidation by-products [4]. Catalytic hydroprocessing is a possible alternative for the disposal of hazardous waste liquids containing toxic or environmental harmful organic chemicals with heteroatoms (Cl, N, O, S) in their chemical structure. The process consists of reacting the organocompounds with hydrogen, yielding hydrogen chloride, ammonia, water, and hydrogen sulphide, respectively, which are easily removed or destroyed, and hydrocarbons, which can be burned or recovered. The process requires a catalyst in order to operate at mild conditions.

A great deal of research has been devoted to hydroprocessing, in particular to hydrodenitrogenation and hydrodesulphurisation processes, that have been investigated in relation to the upgrading of petroleum fractions and coal-derived liquids. In recent years, many investigations have shown that hydrodechlorination is a safe method for the treatment of chlorinated organic waste liquids, although there are important problems concerning to corrosion produced

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by hydrogen chloride and catalyst deactivation caused by fouling and poisoning.

Precious metals (Pd, Pt and Rh) [5,6] and hydrotreatment catalysts (Ni–Mo) [6–8] have shown activity for hydrodechlorination reactions. The most active hydrodechlorination catalysts are supported precious metals, which work satisfactorily at moderate pressure and temperature (1–0.5 MPa, 250 °C). Hydrotreatment catalysts operate at more severe conditions (10 MPa, $T > 350\,^{\circ}C$), being not stable in presence of hydrogen chloride.

In previous studies of our group, it has been observed that supported Pd catalysts are very active and stable for the hydrodechlorination of chloro-aliphatic compounds [9]. Several supports have been tested, the highest activity and stability being obtained with alumina [10]. The influence of process parameters (temperature, pressure, hydrogen flow rate and nature of solvent) on both activity and stability of a Pd/alumina catalyst has been studied; it was found that higher temperature leads to higher initial conversion but faster deactivation, high hydrogen flow rates produce higher conversion and stability of the catalyst, whereas pressure and nature of solvent (toluene or *n*-decane) have no significant effect [11].

However, in order to determine the industrial feasibility of the hydrodechlorination process with Pd/alumina catalysts, the study of the performance of this catalyst in the presence of sulphur compounds, often present in TTCE-containing wastes, is very important. There are very few studies in the literature on the effect of sulphur compounds on hydrodechlorination reactions. Gioia and Murena [12] studied the simultaneous hydrogenation of chlorobenzene, quinoline and methylthiophene on sulphided Ni–Mo on alumina, but the particular effect of S on hydrodechlorination was not considered in detail. Frimmel and Zdrazil [13] studied the parallel hydrogenations of dichlorobenzene and methylthiophene, but their work was focused in comparing the activity of several sulphided transition and precious metals catalysts. To the best of our knowledge, there are no works published dealing with the effect of organosulphur compounds on the hydrodechlorination of aliphatic organochlorinated compounds, and specifically TTCE.

The main aim of this study is to investigate on the effect (poisoning or inhibition) of the presence of sulphur compounds on the hydrodechlorination of TTCE, using a commercial Pd/Al_2O_3 catalyst. For this purpose, TTCE has been catalytically hydroprocessed in the presence of thiophene (TPN), selected as representative of the organosulphur compounds that can be found in real TTCE-containing wastes. The combined hydroprocessing of TTCE–TPN mixtures was compared with the hydrodechlorination of TTCE alone. The influence of the concentration of TPN (0–5 wt.%) and reaction temperature (200–300 °C) has been studied, the reaction kinetics being modelled.

2. Experimental

2.1. Materials

The chemicals used in this work (TTCE, TPN, trichloroethylene—TCE, toluene, methylcyclohexane and decahydronaphthalene) were supplied by Panreac, Fluka and Merck, with a minimum purity of 98%. Hydrogen C-50 was supplied by Air Products with a minimum purity of 99.999%. The catalyst tested was a commercial Pd/Al_2O_3 catalyst (ESCAT 16) supplied by Engelhard, whose composition and textural characteristics are given in Table 1. The catalyst is available in pellets, which were crushed and sieved to a particle size between 0.250 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 internal diameter, 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 was loaded with 0.5 g of catalyst mixed with glass spheres, placed in the mid-section of the reactor. The bottom and top sections were filled with 1 mm glass spheres, the upper glass-bed being used as

Table 1
Composition and textural characteristics of catalyst Engelhard Escat 16

Composition of Pd/Al_2O_3 (wt.%)	0.5
BET specific surface (m^2/g)	92.2
BJH desorption pore volume (cm^3/g)	0.46
Average pore diameter (nm)	18.2

the pre-heating zone. The catalyst was activated in situ before use by passing through the reactor 0.90 l/min (STP) of hydrogen at 350 °C and 0.5 MPa for 6 h. The liquid feed (toluene, TTCE and TPN) flowed downwards through the reactor, pumped by an Alltech 325 liquid chromatography pump. At reaction conditions, the liquid feeds were completely vaporised. Hydrogen was fed 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. This pressure was selected to ensure that most reaction products remained in liquid phase. 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 formed during the reaction. The setup 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 Shimadzu GC-17A apparatus equipped with a FID detector, using decahydronaphthalene as internal standard and an HP-1 30 m capillary column. The oven was maintained at 30 °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 and responses were determined using standard calibration mixtures.

3. Results and discussion

3.1. Determination of the nature of effect of TPN on TTCE hydrodechlorination

The first set of experiments was carried out at 0.5 MPa and 200 and 250 °C, with liquid feed flow rate 0.5 ml/min and hydrogen flow rate 2.3 l/min (STP), which corresponds to 50 times the stoichiometric amount (calculated supposing that TTCE reacts to ethane, TPN reacts to butane and 5% of toluene reacts to methylcyclohexane). In the first part of the experiment, the liquid feed consisted of 10 wt.% TTCE dissolved on toluene. This mixture was fed to the reactor for 50 h. Then, the liquid feed was changed during the next 50 h to 10 wt.% TTCE and 0.5 wt.% TPN dissolved in toluene. Finally, the feed was changed again to 10 wt.% TTCE dissolved in toluene. The reaction products detected by GC-FID were TCE, ethane, butane and methylcyclohexane, whereas the presence of hydrogen chloride and hydrogen sulphide was also detected by chemical methods. These products are formed according to the following reactions:

[A] $C_2Cl_4 + H_2 \rightarrow C_2Cl_3H + HCl$

[B] $C_2Cl_3H + 4H_2 \rightarrow C_2H_6 + 3HCl$

[C] $C_4H_8S + 2H_2 \rightarrow C_4H_{10} + H_2S$

[D] $C_6H_5CH_3 + 3H_2 \rightarrow C_6H_{11}CH_3$

Results, shown in Fig. 1, indicate that TTCE conversion decreases sharply when TPN is added, and then remains constant during the 50 h period in which TPN is fed to the reactor. However, when TPN is removed from the feed, TTCE increases immediately to its initial value. This indicates that, at the studied conditions, TPN is a reversible inhibitor for TTCE hydrodechlorination. On the other hand, the presence

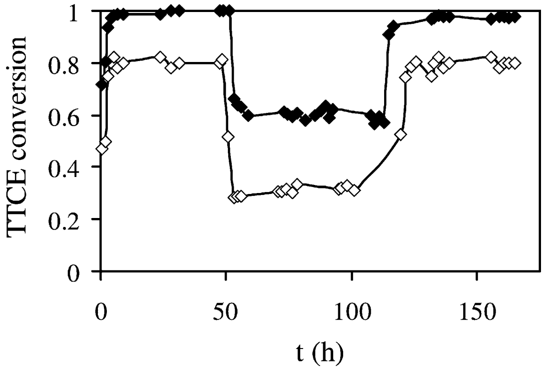

Fig. 1. Evolution of TTCE conversion with time for the hydrodechlorination of 10 wt.% TTCE dissolved in toluene. Space time: 1.8 min g/mmol TTCE. 0.5 wt.% TPN was added during the period 50–100 h. Results at: (◇) 200 °C; (◆) 250 °C.

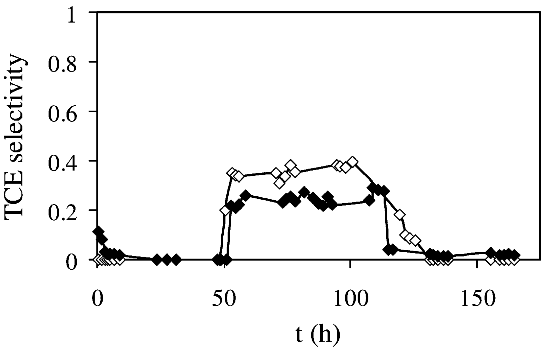

Fig. 2. Evolution of TCE selectivity with time for the hydrodechlorination of 10 wt.% TTCE dissolved in toluene. Space time: 1.8 min g/mmol TTCE. 0.5 wt.% TPN was added during the period 50–100 h. Results at: (◇) 200 °C, (◆) 250 °C.

of TPN produces a big increase in the selectivity for TCE formation (the only partial hydrodechlorination product detected), i.e. from 0% in absence of TPN to 27% for the experiment at 250 °C, when TPN is present (Fig. 2). Consequently, total hydrodechlorination yield decreases strongly. Solvent conversion is very small in all cases (<1%).

3.2. Study of the influence of the temperature and TPN concentration

The effect of temperature on the hydrodechlorination of TTCE–TPN mixtures was studied in the range 200–300 °C, the procedure and reaction conditions being the same as in the previous section. Working at this range of temperatures, we ensure that all reactants are present in the reactor as gases and that the stability of the catalyst is maintained during the experiments (higher temperatures lead to fast catalyst deactivation). Results, shown in Figs. 1 and 3, indicate that the inhibition effect of TPN is stronger at lower temperature: the relative decrease in TTCE conversion in the presence of TPN is 50% at 200 °C, 40% at 250 °C and 32% at 300 °C. This behaviour could be explained considering that TPN is more strongly adsorbed on the catalyst surface at low temperature, resulting a more marked inhibition effect. In the same way, selectivity for TCE formation increases as temperature decreases (39% increase at 200 °C, 27% at 250 °C and 23% at 300 °C, Figs. 2 and 4).

The effect of TPN concentration was studied by feeding the reactor with 10 wt.% TTCE and 0.5, 2.5 or 5 wt.% TPN, dissolved in toluene, working at 0.5 MPa and 250 °C. A constant space time of 1.8 min g/mmol of TTCE was used in all the experiments.

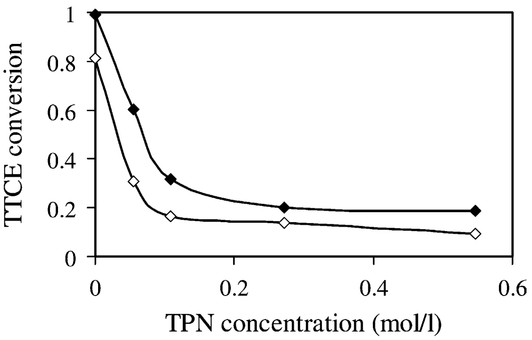

Fig. 3. Influence of TPN concentration on TTCE conversion at different temperatures: (◇) 200 °C, (◆) 250 °C. Space time: 1.8 min g/mmol TTCE.

According to the results, the inhibition effect of TPN is stronger for higher TPN concentrations, up to 2.5 wt.%. For TPN concentrations in the range 2.5–5 wt.%, TTCE conversion remains constant (Fig. 3). On the other hand, higher TPN concentrations lead to higher selectivities for TCE formation (Fig. 4).

3.3. Hydrodesulphuration of TPN

As mentioned previously, the reaction products detected for TPN hydrogenation were butane and hydrogen sulphide. It was found that in all cases, TPN conversion decreased progressively with reaction time,

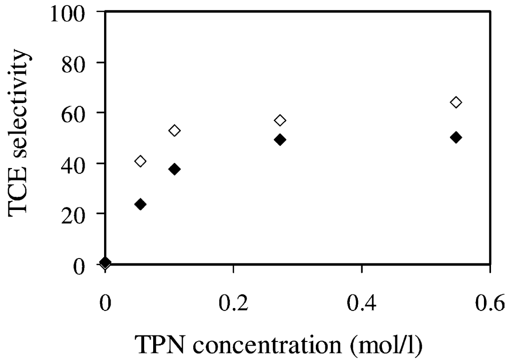

Fig. 4. Influence of TPN concentration on TCE selectivity at different temperatures: (◇) 200 °C, (◆) 250 °C. Space time: 1.8 min g/mmol TTCE.

i.e. from 60% to close to 0% after 50 h (working at 250 °C, for 2.5 wt.% TPN). This behaviour, observed for all temperatures and liquid flow rates studied, was faster for high TPN concentrations. This behaviour is in agreement with other authors, who, working with different reactions, reported that TPN inhibits its own HDS due to the H_2S released [14].

On the other hand, it has been observed that, during the experiments, the reversible inhibition on TTCE hydrodechlorination does not depend on TPN conversion. So, it can be inferred that TPN and H_2S present similar effect on the hydrodechlorination of TTCE.

3.4. Modelling of the reaction kinetics

The kinetics of the hydrodechlorination of TTCE, to form the intermediate TCE and total hydrodechlorination products (reactions [A] and [B]) was studied at 250 °C and 0.5 MPa, charging the reactor with 0.5 g catalyst, and feeding the reactor with 10 wt.% TTCE and 0, 0.5, 1 or 1.5 wt.% TPN, dissolved in toluene. Space times of 0–2.5 min g of catalyst/mmol of TTCE were reached changing the liquid flow rate (0.5–2 ml/min). The $H_2/(\text{TTCE} + \text{TPN})$ molar ratio was maintained constant, resulting an excess of 10:1 over the stoichiometric amount.

The results are shown in Figs. 5 and 6. A decrease in TTCE conversion and an increase in TCE selectivity were observed when TPN concentration increases and space time decreases.

When mixture effects on the kinetics of hydrogenolysis or hydrogenation reactions are considered, the most successful models are often those based on Langmuir–Hinshelwood (LH) mechanisms [15], that have been fitted successfully to the kinetics of the hydrodechlorination of TTCE–TCE–dichloroethylene and TTCE–chlorobenzene mixtures using Pd/Al_2O_3 catalysts [11,16]. Considering the high affinity of hydrogen for the Pd surface, the chemisorption of hydrogen is usually considered as dissociative. Regarding to the adsorption of the organochlorinated and organosulphur compounds, three possibilities can be considered: chemisorption on the same active sites than hydrogen, chemisorption of TTCE and TPN in analogous active sites and hydrogen in a non-analogous site, and chemisorption of hydrogen and TPN in analogous active sites and TTCE in a non-analogous site. The resulting models are usually named Langmuir–Hinshelwood over analogous sites (LHA) and Langmuir–Hinshelwood over non-analogous sites (LHNA1, LHNA2), respectively. Taking into account that hydrogen is present in large excess, and hence its partial pressure is almost constant in all the experiments (0.40 MPa), the kinetic equations derived for LHA and LHNA1 models can be written as

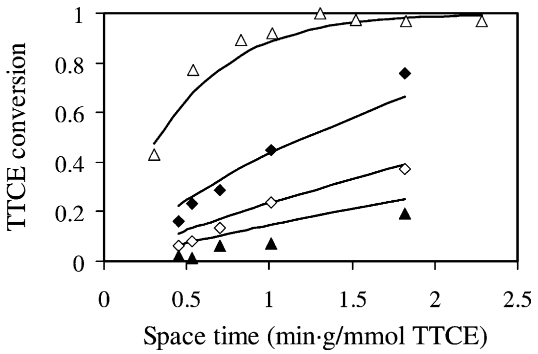

Fig. 5. Evolution of TTCE conversion with space time for the hydrodechlorination of TTCE, for TPN concentrations (wt.%): (△) 0, (◆) 0.5, (◇) 1, (▲) 1.5.

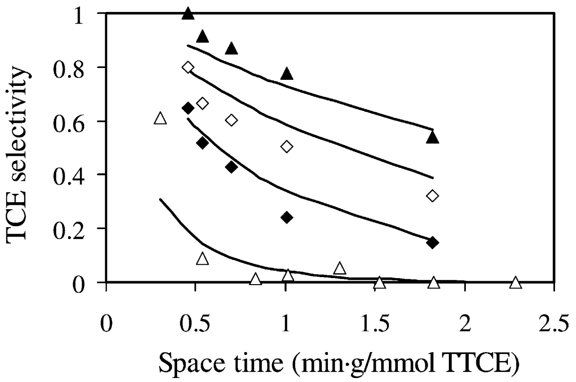

Fig. 6. Evolution of TCE selectivity with space time for the hydrodechlorination of TTCE, for TPN concentrations (wt.%): (△) 0, (◆) 0.5, (◇) 1, (▲) 1.5.

$$(-r_i) = \frac{j'_i p_i}{(1 + K'_i p_i + K'_j p_{j0} + K'_k p_k)^n} \qquad (1)$$

and the kinetic equation derived for LHNA2 model can be written as

$$(-r_i) = \frac{j'_i p_i}{(1 + K'_i p_i + K'_j p_{j0})(1 + K'_k p_k)} \qquad (2)$$

Table 2
Summary of reaction rate models with estimated parameters and correlation coefficients

Model		j_i' (bar^{-1} mol/(min·g))	K_i' (bar^{-1})	r
LHA		$j_i' = \frac{j_i K_i K_H^{1/2} p_H^{1/2}}{(1+K_H^{1/2} p_H^{1/2})^2}$	$K_i' = \frac{K_i}{1+K_H^{1/2} p_H^{1/2}}$	
	TTCE	6.17×10^{-2}	6.64	0.993
	TCE	2.60×10^{-1}	6.64	
	TPN		206.1	
LHNA1		$j_i' = \frac{j_i K_i K_H^{1/2} p_H^{1/2}}{1+K_H^{1/2} p_H^{1/2}}$	$K_i' = K_i$	
	TTCE	6.22×10^{-2}	6.64	0.990
	TCE	2.50×10^{-1}	6.64	
	TPN		965.7	
LHNA2		$j_i' = \frac{j_i K_i K_H^{1/2} p_H^{1/2}}{(1+K_H^{1/2} p_H^{1/2})}$	$K_i' = K_i$	
	TTCE	6.35×10^{-2}	13.29	0.991
	TCE	2.60×10^{-1}	6.64	
	TPN		584.9	

where exponent n is 1 for LHNA1 model and 2 for LHA model; p_i and p_H the partial pressure of component i and hydrogen, respectively; j_i the intrinsic kinetic constant for component i; and K_i and K_H the adsorption constants for component i and hydrogen, respectively. The constants j_i' and K_i' are defined in Table 2 for the models considered. In these equations, i represents TTCE, k represents TCE, and j represents the sum of the concentration of TPN and H_2S in the reactor. The sum of these concentrations remains constant during the reaction and equal to TPN initial concentration, given the reaction stoichiometry; it has been demonstrated in the experiments that the effect of TPN and H_2S on TTCE hydrodechlorination is the same, so we consider both effects in the same parameter (K_j).

Reactions [A] and [B] are assumed to follow serial kinetics. Other assumptions considered are PFR-like behaviour, reactants in gas phase and diffusion and thermal effects negligible. PFR-like behaviour (by-pass and axial dispersion effects negligible) can be considered when (reactor diameter/particle diameter) >10 and (catalytic bed length/particle diameter) >50 [17]. In our case, the values of these ratios are 18 and 100, respectively. The presence of the reactants in gas phase at reaction conditions has been demonstrated through thermodynamic calculations using simulation programs as HYSIM (Uniquac model). It has been also demonstrated that there is no influence of mass-transfer and heat-transfer limitations, as the Damköhler and Wheeler-Weisz (defined as Thiele modulus multiplied by the overall inter–intraphase isothermal effectiveness) numbers are nearly zero [18].

The kinetic parameters for the three models were calculated by fitting the corresponding rate expressions to the experimental data by means of non-linear least squares minimisation of the error in the prediction of conversions, using a simplex algorithm followed by a Powell minimisation algorithm. The differential equations were integrated using the EPISODE package. These mathematical tools are implemented in the commercial programme Scientist. The quality of the fitting was quantified using the correlation coefficient (r).

Results are given in Table 2. Although the r values and the values of the constants are very similar in all the model proposed, the LHA model seems to be the most appropriate since the discrepancy between experimental and model points is the lowest and the postulates of this model are in a better agreement with previous works [15,16]. In this works, it was observed that chloroolefins and hydrogen are chemisorbed in the same active sites. Experimental (points) and predicted (lines) values for TTCE conversion and TCE selectivity for this model are given in Figs. 5 and 6. It can be observed that the fitting for the proposed model is fairly good. It is also observed that the model also predicts the "saturation effect" of the sulphur compounds. So it should be noted that the conversions predicted by the model for the two highest concentrations are nearer than in the case of the lowest additions of sulphur.

These results agree with previous works of our group on the hydrodechlorination of mixtures containing aliphatic organochlorinated compounds [15] and mixtures of aliphatic and aromatic compounds [16]. The tendency of the calculated constants is in good agreement with the experimental observations: TPN presents higher inhibition capacity than TTCE, as shown by its higher adsorption constant.

4. Conclusions

The presence of TPN leads to a reversible inhibition of the hydrodechlorination reaction of TTCE over a commercial Pd/Al_2O_3 catalyst, and increases strongly the selectivity for TCE formation, decreasing the total hydrodechlorination yield. This effect is stronger at low temperature and high concentration of TPN, saturation being observed for TPN concentrations higher than 2.5 wt.%. The kinetic analysis of the reaction, that can be modelled by a Langmuir–Hinshelwood mechanism, considering adsorption of H_2 (dissociative), TPN and TTCE on the same active site, confirm that the inhibition effect of TPN can be explained by competitive adsorption.

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