

# Catalytic hydrodechlorination of tetrachloroethylene over red mud

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## Abstract

Hydrodechlorination of tetrachloroethylene was investigated using red mud (RM, a by-product in the production of alumina by the Bayer process) as the catalyst. Use of RM as a hydrodechlorination catalyst is of interest from an industrial point of view because its cost is much lower than that of commercial catalysts.

Hydrodechlorination reactions were carried out in a continuous fixed bed reactor. The influence of catalyst sulfiding, temperature (50–350°C), pressure (2–10 MPa), hydrogen flow rate and the presence of solvents (hexane, heptane, benzene and toluene) on the reaction was studied. Sulfided red mud is active as a hydrodechlorination catalyst, conversion of tetrachloroethylene increases as the pressure and temperature increase. The solvents did not influence the conversion, nor were side reactions involving the solvent observed.

The kinetics of the reaction was studied at 350°C and 10 MPa, conditions for which mass transfer limitations were negligible. A good fit of a Langmuir–Hinshelwood model to the experimental data was obtained. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Hydrodechlorination; Hydrogenolysis; Tetrachloroethylene; Red mud; Iron sulfide catalysts

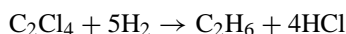
## 1. Introduction

The destruction of hazardous organochlorinated compounds is a very important environmental problem. In particular, tetrachloroethylene (TTCE, also called perchloroethylene, per or tetrachloroethene) is the organochlorinated compound that is released into the atmosphere in the greatest quantity according to the EPA reports [1]. TTCE is carcinogenic for humans and very harmful for the environment, being involved in smog formation and global warming [2]. However, its physical and chemical properties (it is not flammable and

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it is an efficient solvent for greases and many organic compounds) make this compound difficult to replace in many applications, especially in dry-cleaning. Because of the high organic chlorine content of these wastes, incineration is expensive (temperatures higher than 900°C are required) and constitutes a potential environmental hazard since highly dangerous by-products, such as phosgene, dibenzofuranes and dioxins, can be formed during the oxidation. Furthermore, this process requires extensive consumption of energy [3].

Catalytic hydrodechlorination is an attractive alternative to thermal incineration for the abatement of organochlorinated pollutants, because hydrodechlorination occurs at lower temperatures and because it transforms the organochlorinated compounds into less harmful chlorine-free organic compounds that can be safely recovered or burned. In addition, the hydrogen chloride can easily be removed from the product stream by alkaline washing. Kalnes et al. [4] have demonstrated the advantage of catalytic hydrodechlorination relative to thermal incineration with regards to energy consumption. The complete hydrodechlorination of TTCE is described by the following stoichiometry



Hydrodechlorination of most organic compounds, including TTCE, requires the presence of a catalyst if appreciable yields are to be obtained under reasonable conditions [5]. The most widely tested catalysts for hydrodechlorination reactions are supported precious metals, such as palladium, platinum and rhodium. These catalysts present the disadvantages of being both expensive and very susceptible to poisoning by hydrogen chloride and organic impurities such as organosulfur and organonitrogen compounds, which could potentially be present in organic waste streams resulting from use of TTCE and other chlorinated solvents as cleaning agents.

Sulfided transition metal catalysts are widely used in hydrotreating organic fractions and are also resistant to poisons. Because of similarities between the mechanisms of hydrodesulfurization–hydrodenitrogenation and hydrodechlorination reactions, these sulfided catalysts have been proposed as catalysts for hydrodechlorination [6,7]. Typical hydrotreating catalysts, such as Ni/Mo, have been used in the hydrodechlorination of polychlorobenzenes [8,9], polychloroethylenes [7], polychloromethanes [10] and in combined hydrodesulfurization–hydrodechlorination [11]. However, chlorine is an effective poison for these catalysts [12,13] and although the hydrotreating catalysts are cheaper than precious metals, they are still expensive.

Red mud (RM) could be an interesting alternative to these commercial scale catalysts for hydrodechlorination reactions. RM is a by-product in the manufacture of alumina by the Bayer process, but has little or no commercial value. This material consists primarily of oxides of iron, aluminium, titanium, but contains smaller amounts of oxides of silicon, calcium and sodium. Sulfided RM is active as a hydrogenation catalyst because of its iron sulfide content. This material has been used for the hydrogenation of polyaromatic compounds [14] and the liquefaction of coal [15]. Iron sulfide catalysts have also been used in hydrodesulfurization reactions [16]. In addition, Frimmel and Zdrzil claim that all transition metal sulfides are active to some extent for the hydrodechlorination of chlorobenzene [17].

The use of sulfided RM as a catalyst for the hydrodechlorination of TTCE was investigated in this study. The influence of catalyst sulfiding, temperature, pressure, hydrogen flow rate

and the presence of different solvents were studied. Finally, a kinetic model of the general Langmuir–Hinselwood form was developed to fit the kinetic data.

## 2. Experimental

### 2.1. Materials

The chemicals used in this study (TTCE, carbon disulfide, toluene, benzene, *n*-hexane, *n*-heptane and cycloheptane) were supplied by Panreac and Merck. These products were characterized by minimum purity of 99.5%. The RM was supplied by the San Ciprián (Lugo, Spain) plant of the Spanish aluminium company Inespal. RM is the residue of the caustic digestion of bauxite. Consequently, it contains all the elements present in bauxite that are insoluble or only partially soluble in sodium hydroxide (Fe, Ti, Al and Cr, K, Mg, Mn, Ce, Ga, La, and Y at smaller concentrations), plus sodium and calcium originated from the reagents added during the leaching process. The RM was analyzed by atomic absorption spectrometry and volumetric methods after dissolution in acid or after alkaline fusion, depending on the element analyzed. The surface composition (1  $\mu\text{m}$  in depth) of the RM was determined using the X-ray microanalyzer of an electron scanning microscope (JSM 6100). For this analysis, catalyst samples must be polished and carbon coated. The compositions of the catalysts obtained by both methods are given in Table 1. The composition of the RM could depend on the bauxite ore from which it was derived. In our experiments we have used two different materials, both originating from Inespal. There were no significant differences in the compositions of these materials. The compositions of other RMs described in the literature are similar, with the main constituents (Fe, Al, Ti, Si, Ca and Na) being the same [18]. Although, small differences may exist in the concentration of these elements, the concentration of iron (which is assumed to be the active metal) is in all cases in the range 19–23 wt.%.

The catalyst pore structure and surface area were measured by nitrogen adsorption with a Micromeritics ASAP-2000 apparatus. Morphological parameters for both the RM and the sulfided RM are given in Table 2. The following mineralogical RM constituents were

Table 1  
Bulk and EDX composition of red mud

Element	Bulk composition (wt.%)	EDX composition (wt.%)
Fe	19.07	21.7
Ti	13.0	11.9
Al	7.9	7.4
Na	3.7	3.0
Ca	5.1	4.9
Si	4.7	3.6
P	–	0.7
V	–	0.3
Cl	–	0.3

Table 2  
Surface parameters of the fresh and sulfided red mud

Parameter	Fresh red mud	Sulfided red mud
Specific surface (m <sup>2</sup> /g) <sup>a</sup>	24.3	29.5
Pore volume (cm <sup>3</sup> /g) <sup>b</sup>	0.086	0.090
Average pore diameter (nm) <sup>c</sup>	12.1	10.5

<sup>a</sup> Determined by the method of Brunauer, Emmet and Teller (BET).

<sup>b</sup> Determined by the method of Barret, Joyner and Halenda (BJH).

<sup>c</sup> Determined by the method of Kelvin.

identified by X-ray diffraction (XRD): rutile, TiO<sub>2</sub>; hematite, Fe<sub>2</sub>O<sub>3</sub>; goethite and lepidocrocite, FeO(OH); iron hydroxide Fe(OH)<sub>3</sub>; halloysite, Al<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>(OH)<sub>4</sub> and bayerite, Al(OH)<sub>3</sub>. After the RM was sulfided, the RM percentage of crystalline iron oxides and hydroxides decreases sharply and formation of pyrrhotite, Fe<sub>8</sub>S<sub>9</sub> was observed.

## 2.2. Experimental apparatus

All experiments were carried out in a continuous flow fixed bed reactor. The reactor was a stainless steel cylinder (9 mm i.d. and 45 cm long) placed inside a tubular electrical furnace. Five thermocouples were used to monitor the temperature at different positions. An amount of 2 g catalyst (particle size 50–100 μm), diluted with inert alumina, were placed in the mid-section of the reactor. The lower and upper regions of the tube were packed with low surface area inert alumina (100–200 μm), the upper bed of alumina being used as a preheating zone.

The liquid feed consisted of 10% (w/w) TTCE dissolved in *n*-hexane (or in another organic solvent when the effect of the solvent was studied). The feed was supplied by a liquid chromatography pump and flowed downwards through the packed bed. Hydrogen was fed co-currently at a flow rate governed by a mass flow controller.

The distribution of liquid and gas phases in the reactor under reaction conditions was studied by calculating the relevant vapor–liquid equilibria using the simulation program HYSIM and the thermodynamic model UNIFAC. Except for the studies of the influence of temperature on TTCE conversion, only a gas phase was present in the reactor. However for the studies carried out at temperatures lower than 250°C and a pressure of 10 MPa, both liquid and gas phases were present in the reactor.

The reaction products were collected in a cylindrical receiver connected to a back-pressure regulator that maintained the operating pressure by venting the excess gas. Liquid samples were taken by emptying the receiver at selected time intervals. The apparatus was equipped with safety features such as temperature and pressure controllers and a rupture disc. A schematic diagram of the reactor is shown in Fig. 1.

Catalysts sulfiding was performed in situ prior to use of the catalyst by passing a mixture of 10% (v/v) H<sub>2</sub>S in H<sub>2</sub> at atmospheric pressure over the catalyst at 400°C, at a flow of 3 l/h for 4 h. The sulfiding temperature was chosen on the bases of the observations of Ramselaar et al. [19], who indicated that at sulfiding temperatures above 400°C, elemental sulfur is formed, blocking access to the iron sulfide active centers. In some experiments,

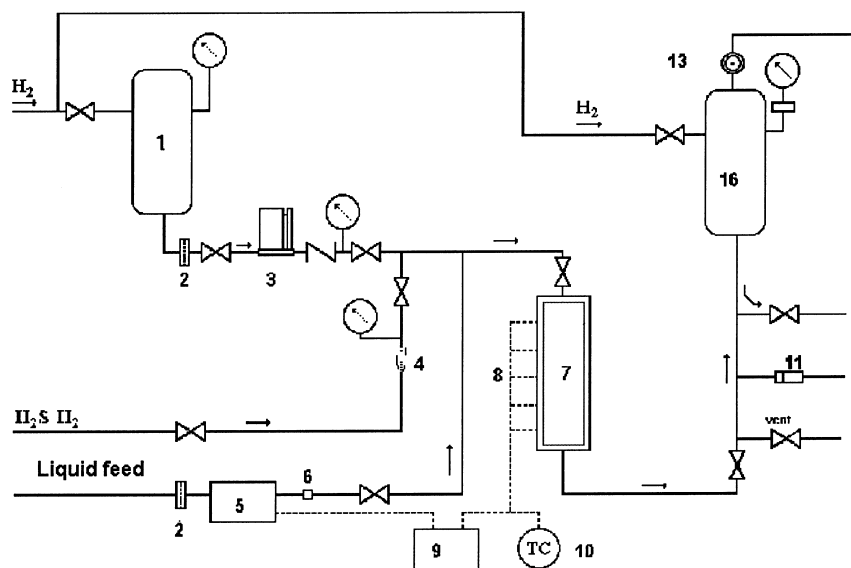


Fig. 1. Schematic diagram of the hydrodechlorination reactor: (1) hydrogen cylinder; (2) filter; (3) mass-flow regulator; (4) rotameter; (5) liquid pump; (6) pulse damper; (7) reactor; (8) thermocouples; (9) recorder; (10) temperature controller; (11) rupture disk; (12) receiver and (13) back pressure regulator.

carbon disulfide was added to the liquid feed to maintain the catalyst in sulfided form. Under reaction conditions, carbon disulfide is almost instantaneously hydrogenated to hydrogen sulfide and methane.

An initial experiment was carried out at 10 MPa and 400°C with the reactor filled only with  $\alpha$ -alumina. The liquid feed consisted of a solution of 10% (w/w) TTCE in hexane. TTCE conversion was negligible for all liquid flow rates tested (0.4–3 ml/min). In subsequent experiments, the reactor was charged with 2 g of RM. The effect of sulfiding the catalyst prior to use was studied with the same feed at 350°C and 10 MPa, RM being either unsulfided or sulfided via the method noted above. Studies of the influence of addition of CS<sub>2</sub> were carried out at 350°C, 10 MPa, 0.7 ml/min of 10% TTCE dissolved in hexane and CS<sub>2</sub> concentrations of up to 2.5% (w/w). The influence of operating conditions (temperature, pressure and hydrogen flow) was studied in the following sets of experiments, carried out in the presence of CS<sub>2</sub> and hexane as solvent: 10 MPa, 0.8N l/min of H<sub>2</sub>, temperature 75–350°C; 350°C, 0.8N l/min, pressure 2–10 MPa; 350°C, 10 MPa, hydrogen flow rate 0.4–1.4N l/min. Kinetic studies were also carried out in the presence (1%) and absence of CS<sub>2</sub> and using hexane as solvent at 350°C, 10 MPa, a hydrogen flow rate 0.8N l/min and space times 1–18 (min g catalyst)/(mmol of TTCE).

In the kinetic studies, reactions were conducted for an initial period of 5 h without taking samples so that the catalysts could reach a constant activity level. To avoid transient effects, samples taken after changes in the liquid or gas flow rates, solvent, temperature or pressure were discarded.

### 2.3. Analysis

The reaction products were analyzed in a Hewlett-Packard Model 5890 gas chromatograph equipped with an FID detector and a 60 m VOCOL fused silica capillary column. Cycloheptane was employed as an internal standard. The temperature was maintained at 35°C for an initial period of 15 min and then increased to 180°C at a rate of 6°C/min. Analyses were carried out in split mode. Peak assignments were made using GC–mass spectra (Finnigan GCQ). The hydrogen chloride content of the vent gases was analyzed by absorption in water, followed by titration with sodium hydroxide. In all the experiments, the only reaction products detected were ethane and hydrogen chloride. Neither chlorinated compounds (organic or inorganic), cracking by products nor products resulting from hydrogenation of the solvent were detected in the product stream. The chlorine mass balance was checked to ensure the absence of other reaction products. Even in the worse cases, closures in excess of 95% were obtained

## 3. Results and discussion

### 3.1. Effects of sulfiding the catalyst and adding of CS<sub>2</sub>

TTCE conversions for both unsulfided and sulfided RM after 1 h reaction time (see Fig. 2) indicate that the catalyst is more active in the sulfided form, especially at higher space times. In addition, inspection of the deactivation curves (Fig. 3) indicates that the unsulfided RM suffers rapid deactivation. Activity of Ni/Mo catalysts as oxides has also been reported by Gioia et al. for the hydrodechlorination of chlorobenzenes [9,20] and by Martino et al. for the hydrodechlorination of dichloromethane, trichloroethylene and tetrachloroethylene [13].

Subsequently, CS<sub>2</sub> was added to the feed in order to maintain the catalysts in the sulfided form. However, this positive effect may be overridden by the inhibitory effect of the H<sub>2</sub>S formed under reaction conditions. Murena et al. [21] reported that the optimum concentration of CS<sub>2</sub> for hydrodechlorination of trichlorobenzene with sulfided Ni/Mo was 0.3% (w/w), while Hagh and Allen [22] stated that the addition of CS<sub>2</sub> has a negative effect on hydrodechlorination reactions with a similar catalyst. Conversions obtained after 4 h

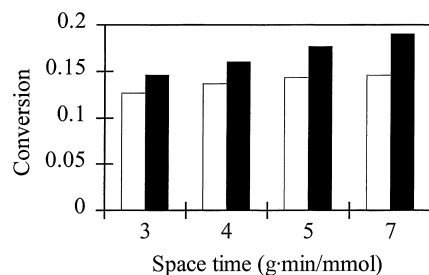


Fig. 2. Effect of sulfiding the catalyst, used in the hydrodechlorination of TTCE at different space times: white area, unsulfided; shaded area, sulfided. Experiments at 350°C, 10 MPa, 0.8Nl/min and without CS<sub>2</sub> in the feed.

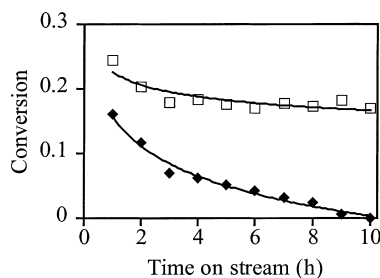


Fig. 3. Deactivation curve for sulfided (□) and unsulfided (◆) red mud. Experiments at 350°C, 10 MPa, 0.8N l/min, 7 g min/mmol and without CS<sub>2</sub> in the feed.

reaction time are depicted in Fig. 4. The presence of carbon sulfide at concentrations lower than 1.5% does not significantly affect the conversion, whereas higher amounts cause a significant decrease in catalyst activity. Consequently, 1% (w/w) of CS<sub>2</sub> was added to the feed in the subsequent experiments.

### 3.2. Effect of temperature

Results of the effect of temperature (75–350°C at 100 bar) on catalyst performance are represented in Fig. 5. A strong dependence of the conversion on temperature can be observed, the highest conversion being attained at the highest temperature tested, i.e. 350°C. The sharp increase in TTCE conversion for temperatures higher than 250°C may be partially caused by the complete disappearance of the liquid phase within the reactor at these conditions (the reaction mixture is completely in gaseous phase). Hence, resistance to mass transfer is reduced and the reaction rate is faster.

It is important to note that the selectivity towards ethane was always higher than 99%, no partially dechlorinated compounds were detected, even at very low TTCE conversions (only non-quantifiable concentrations of trichloroethylene and dichloroethylene isomers were found by mass spectrometry). By contrast, Kim and Allen [7] reported higher activities but also higher selectivities for chlorinated compounds (up to 20%) for the hydrodechlorination

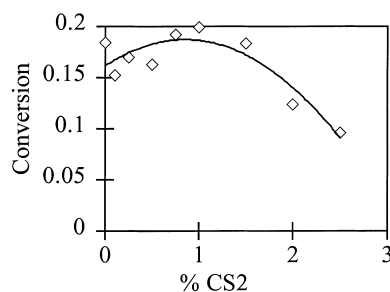


Fig. 4. Effect of addition of CS<sub>2</sub> on the performance of the sulfided red mud used as a catalyst for TTCE hydrodechlorination.

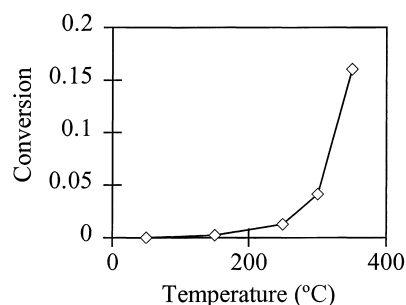


Fig. 5. Conversion for the catalytic hydrodechlorination of TTCE at 10 MPa and 0.8N l/min of H<sub>2</sub> vs. reaction temperature.

of TTCE over a sulfided Ni/Mo catalyst under similar operating conditions. This aspect may be partially explained by considering the difference in the catalytically active phases. In the case of the Ni/Mo catalyst, the catalytic phase is more active (higher conversions), but the concentration of the active phase is lower, a situation which can lead to lower selectivity.

### 3.3. Effect of pressure and hydrogen flow rate

The dependence of the catalyst performance on total pressure (2–10 MPa at 350°C and 0.8N l/min of H<sub>2</sub>) and hydrogen flow rate (0.4–1.4N l/min at 350°C and 10 MPa), can be observed in Table 3. For hydrogen flow rates lower than 0.6N l/min, reaction rate increases as the flow rate increases. This result indicates that the reaction rate is influenced by gas-catalyst particle mass transfer. For hydrogen flow rates higher than 1N l/min, the reaction rate increases for increasing partial pressure of TTCE and hydrogen. The highest conversion was attained at 350°C and 10 MPa, conditions at which subsequent experiments were carried out. Similar reaction conditions are reported in the literature for hydrodechlorination reactions over hydrotreating catalysts [7,13,19].

Table 3  
Experimental results of the studies about the influence of pressure and hydrogen flow

Total pressure (MPa)	H <sub>2</sub> flow (Nl/min)	TTCE initial partial pressure (MPa)	H <sub>2</sub> initial partial pressure (MPa)	Conversion
10	0.4	0.119	7.68	0.082
10	0.5	0.101	8.04	0.143
10	0.6	0.084	8.37	0.181
10	0.8	0.067	8.69	0.183
10	1	0.055	8.92	0.184
10	1.2	0.047	9.09	0.169
10	1.4	0.041	9.21	0.152
8	0.8	0.054	6.95	0.12
6	0.8	0.041	5.21	0.087
4	0.8	0.027	3.48	0.037
2	0.8	0.012	1.74	0.017



### 3.4. Effect of solvent

Industrial wastes containing TTCE usually contain non-chlorinated organic compounds, such as spent solvents or fats. In some cases a solvent should be added to facilitate handling. Organic compounds can affect the hydrodechlorination process, e.g. by reacting and hence consuming hydrogen or competing for the catalytic sites with TTCE. Thus, the effects on of the presence of four widely used solvents on in the TTCE hydrodechlorination was studied. The solvents, both aliphatic and aromatic, were benzene, toluene, hexane and heptane. TTCE conversions attained after 2 h reaction time for the solvents tested were: hexane, 18.5%; heptane, 18.9%; benzene, 17.9%; toluene, 18.2%. These results indicate that the influence of the solvent on the conversion is negligible. Moreover, the reaction products contained no compounds that could have been formed by hydrogenation or cracking of any of these solvents. This result constitutes an important difference between the catalytic properties of sulfided RM and alumina-supported hydrotreating catalysts. The latter material produces appreciable amounts of substances formed by cracking and hydrogenation reactions of the indicated solvents [13]. This difference in behaviour can be explained by considering the low surface acidity of sulfided RM compared with that of hydrotreating catalysts supported on  $\gamma$ -alumina [23,24]. Experiments carried out in presence of  $\gamma$ -alumina under the same operating conditions produced appreciable amounts of products formed by cracking reactions of the solvents, for example, light hydrocarbons.

### 3.5. Kinetic experiments

The kinetics of hydrodechlorination of TTCE over sulfided RM was studied for liquid feeds both containing and not-containing 1% (w/w) carbon disulfide. Both gas-particle and intra-particle diffusion effects were negligible under the experimental conditions employed, according with the criteria of Carberry [25] (Damköhler number  $Da = 0.004$ , Weisz number  $We = 0.006$ ). Furthermore, at these values of  $Da$  and  $We$ , nonisothermal effects are also negligible. Moreover, plug flow behaviour can be assumed, since the ratio of the reactor diameter to the diameter of the catalyst particle is 36 and the ratio of the reactor length to particle diameter is 200 [25].

Conversions of TTCE as a function of space time are shown in Fig. 6. Comparison of results obtained in the presence and absence of carbon sulfide confirms the positive effect of addition of carbon disulfide to the feedstock on catalyst performance.

Hydrodechlorination of polychloroethylenes has been proposed to follow a mechanism consisting of successive hydrogenation of the double bond followed by elimination of hydrogen chloride, the first hydrogenation step being rate controlling [10,26]. Many kinetic models have been proposed for the hydrogenation of double bonds over sulfides [27], the most successful ones corresponding to the Langmuir–Hinselwood type. Similar models have been used to model the kinetics of hydrodesulfurization and hydrodenitrogenation over sulfide catalysts [28,29] and for hydrodechlorination, (especially when organochlorinated molecules containing olefinic or aromatic structures are involved), over precious metals [30–32] and hydrotreating catalysts [8].

Adsorption of hydrogen is generally admitted to be dissociative over noble metal catalysts, but for sulfided catalysts there is controversy about the nature of the adsorption, many authors

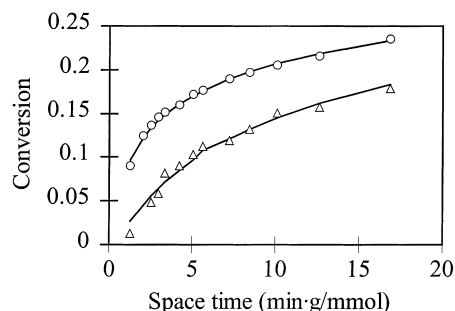


Fig. 6. Experimental conversion and calculated profiles for the catalytic hydrodechlorination of TTCE at 350°C, 10 MPa and 0.8Nl/min of H<sub>2</sub>, as a function of TTCE space time for a feed without CS<sub>2</sub> (Δ) and with 1% CS<sub>2</sub> (○).

considering it to be associative [27,28]. Other researchers consider the inhibition caused by the hydrogen chloride generated in the reaction, especially for catalysis by supported noble metals [32]. However, the interaction of hydrogen chloride with pyrrhotite (a gas–solid reaction) is chemically different from its interaction with noble metals (adsorption).

Different kinetic expressions were fit to the experimental data, the best fit was obtained with a Langmuir–Hinselwood rate expression, in which only adsorption of TTCE and hydrogen (non-dissociative) is significant. These species are presumed to adsorb on the same active sites. The elementary steps involved in the reaction mechanism are the following

- (i) TTCE +  $\sigma \leftrightarrow$  TTCE- $\sigma$  (adsorption equilibrium for TTCE)
- (ii) H<sub>2</sub> +  $\sigma \leftrightarrow$  H<sub>2</sub>- $\sigma$  (adsorption equilibrium for H<sub>2</sub>)
- (iii) TTCE- $\sigma$  + H<sub>2</sub>- $\sigma \rightarrow$  CCl<sub>2</sub>H-CCl<sub>2</sub>H- $\sigma$  +  $\sigma$  (rate controlling reaction)
- (iv) CCl<sub>2</sub>HCCl<sub>2</sub>H- $\sigma \rightarrow$  CCl<sub>2</sub>=CHCl- $\sigma$  + HCl (fast reaction)
- (v) CCl<sub>2</sub>=CHCl- $\sigma$  + 4H<sub>2</sub>- $\sigma \rightarrow$  C<sub>2</sub>H<sub>6</sub>- $\sigma$  + 3HCl (fast consecutive reactions)
- (vi) C<sub>2</sub>H<sub>6</sub>- $\sigma \rightarrow$  C<sub>2</sub>H<sub>6</sub> (desorption, fast)

The reaction (v) must actually consist of a series of steps, all of which are fast.

The rate of disappearance of TTCE ( $-r_{\text{TTCE}}$ , mmol TTCE/g catalyst s) is

$$-r_{\text{TTCE}} = \frac{kK_{\text{TTCE}}K_{\text{H}_2}p_{\text{TTCE}}p_{\text{H}_2}}{(1 + K_{\text{TTCE}}p_{\text{TTCE}} + K_{\text{H}_2}p_{\text{H}_2})^2} \quad (1)$$

where  $k$  (mmol TTCE/g catalyst s) is the intrinsic rate constant for the rate controlling reaction and  $K_{\text{TTCE}}$  and  $K_{\text{H}_2}$  (MPa<sup>-1</sup>) the adsorption equilibrium constants for TTCE and hydrogen.

If the catalytic bed is treated as a PFR reactor, the reaction rate, TTCE conversion ( $x$ ) and space time ( $\tau$ , min g catalyst/mmol TTCE) are related by

$$\frac{dx}{d\tau} = -r_{\text{TTCE}} \quad (2)$$

Table 4

Kinetic parameters for the hydrodechlorination of TTCE over sulfided red mud in presence (a) and absence (b) of carbon sulfide<sup>a</sup>

	Presence	Absence
$k$ (mmol/g min)	$1.3 \pm 0.02$	$0.15 \pm 0.01$
$K_A$ (MPa <sup>-1</sup> )	$147.1 \pm 1.6$	$53.6 \pm 3.0$
$K_H$ (MPa <sup>-1</sup> )	$1.6 \pm 0.2$	$9.1 \pm 1.2$
$r^2$	0.998	0.996

<sup>a</sup> Confidence limits are referred to 99%.

Kinetic parameters were obtained by numerical integration of Eq. (1) and (2) and the integrated equation was fit to the experimental results using the computer program Scientist.

As mentioned previously, under the reductive conditions at which the reaction is carried out, the primary catalytically active phase is pyrrhotite [16], a non-stoichiometric sulfide, which has a variable Fe/S stoichiometry depending on temperature and hydrogen sulfide partial pressure [20]. Because the phases constituting pyrrhotite have different crystallographic properties and hence different catalytic properties, the kinetic parameters were calculated independently for the experimental data sets obtained in the presence and absence of carbon disulfide. Results are shown in Table 4. The good agreement between the experimental and calculated results can be observed in Fig. 6. The values calculated for the TTCE adsorption constant, and especially the kinetic constant, are higher for the experiments in which CS<sub>2</sub> was present in the feed. The hydrogen adsorption constant is also slightly larger. These results can be explained by the changes in the active phase induced by the presence of H<sub>2</sub>S.

Alternative kinetic models were also considered. If the chemisorption of hydrogen sulfide (in the case of the experiment with CS<sub>2</sub> in the feed) is taken into account, the calculated values of the kinetic parameters ( $k$ ,  $K_{TTCE}$  and  $K_{H_2}$ ) were very similar to those attained when the adsorption of H<sub>2</sub>S was not considered and being the value of adsorption constant for H<sub>2</sub>S very closed to zero. If dissociative adsorption of hydrogen or hydrogen and TTCE adsorption

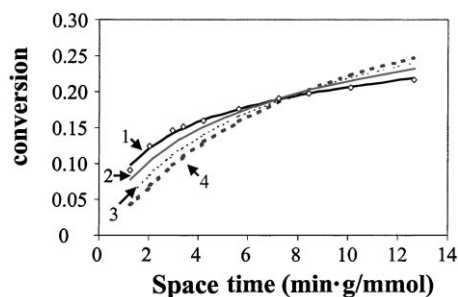


Fig. 7. Experimental conversion ( $\diamond$ ) and predicted trend according to: (1) Langmuir–Hinselwood model which considers competitive adsorption on the same type of active sites (the chemisorption of the H<sub>2</sub> is associative); (2) Langmuir–Hinselwood model which considers competitive adsorption on the same type of active sites (the chemisorption of the H<sub>2</sub> is dissociative); (3) Langmuir–Hinselwood model which considers adsorption on two different types of active sites (the quality of the fit of this model is essentially the same, regardless of whether the chemisorption of H<sub>2</sub> is associative or dissociative) and (4) pseudo-first order kinetics.

on different active sites are considered, the fits of these models to the experimental results were of poorer quality (Fig. 7). Models which take into account adsorption of hydrogen chloride, lead to inconsistent results and negative values of the kinetic parameters.

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