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Hydrodechlorination of tetrachloroethylene over sulfided catalysts: kinetic study

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Abstract

In this work, a commercial sulfided hydrotreatment catalyst (2.8% NiO, 13.5% MoO_3, supported on γ-alumina, supplied by Shell) is compared with different iron sulfide based catalysts. These catalysts were prepared from a by-product (called red mud (RM)) of the bauxite leaching in the Bayer process. Two different activation procedures were tested, both based in dissolving the RM in an acid solution (HCl or HCl + H_3PO_4) followed by a precipitation with ammonia at $pH = 8$ and calcining at 500 °C. All the catalysts were sulfided at 400 °C.

The commercial catalyst was more active than the iron sulfide catalysts in all the range of space times tested. However, considering the low prize of the RM based catalysts, they could be an interesting alternative to the hydrotreatment catalysts. The selectivity for ethane was near 100% for all the catalysts tested.

Kinetics results were successfully modeled with a Langmuir–Hinshelwood model, assuming that the chemisorption of hydrogen (considered as associative) and TTCE occurs over analogous active sites. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hydrotreatment catalysts; Iron sulfide catalysts; Hydrodechlorination; Tetrachloroethylene; Reaction kinetics

1. Introduction

Chlorinated organic solvents, specially tetrachloroethylene (TTCE), are widely used in many industries, being the main applications dry-cleaning and preparation of textile fibers, degreasing of metals, extraction of organic compounds and cleaning of electronic devices. Organic wastes with high content in TTCE are produced in these uses, being the disposal of these wastes a major environmental and social problem because of the TTCE toxicity and its capability for accumulating in the environment for long time [1].

Catalytic hydrodechlorination has been shown to be an environmentally and economically effective way to destroy organochlorinated pollutants in organic media [2,3]. In this process only hydrogen chloride and hydrocarbons are produced, no harmful by-products such as phosgene or dioxins being formed.

The most important issue in catalytic hydrodechlorination is catalyst selection. Supported precious metal catalysts are very sensible to poisoning by impurities in the feed [4], whereas the hydrotreatment ones are very sensible to the poisoning caused by hydrogen chloride [5]. Both kinds of catalysts are expensive. Because of these reasons, the development of cheap, disposable catalysts would be very interesting.

Red mud (RM) is a by-product in the manufacture of alumina by the Bayer process, specifically the solid residue of the caustic leaching of bauxite. Its main constituents are iron, titanium and aluminum oxides, with a significant content of silicon, calcium and sodium

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oxides. RM is produced as a residue in great amounts, and its storage is an important environmental problem. When RM is sulfided (SRM), iron oxides are transformed into pyrrhotite, a non-stoichiometric sulfide, thermodynamically stable at temperatures above 200 °C, nominally Fe_7S_8, with a regular NiAs structure [6]. This structure has "iron vacancies" (formed due to its non-stoichiometric character), which exhibit spatial order. Pyrrhotite has been shown to be catalytically active in reactions involving the activation of hydrogen, such as coal liquefaction [7] or tiophene hydrodesulfuration [8].

In previous works, a significant catalytic activity of SRM for the hydrodechlorination of TTCE was observed at typical hydrotreating conditions (10 MPa and 350 °C) [9]. However, SRM suffered fast deactivation, mainly caused by a strong HCl poisoning, that destroyed the crystallographic structure of pyrrhotite [10]. In these works, it was observed that the addition of small amounts of CS_2 to the reaction feed improved the catalyst performance (life and activity).

Several methods have been proposed in the literature for enhancing the catalytic activity of RM. Pratt and Christoverson [11] proposed a dissolution–precipitation method (basically, dissolution of the RM in hydrochloric acid and precipitation with ammonia at $pH = 8$), which decreases the Ca and Na RM content, and increases its specific surface. RM modified by the method of Pratt and Christoverson will be referred to in this work as "activated RM", ARM. Sulfided activated red mud (SARM) was tested as a catalyst for the hydrogenation of anthracene oil [12], and was found to be more active than untreated sulfided RM for this reaction. In addition, it presents an extended active life.

In a previous work of our group, a new activation method for RM, based on the method of Pratt–Christoverson, was presented. The modified activation method consists is the addition of *ortho*-phosphoric acid to the hydrochloric acid for the leaching of the RM. It was found that the addition of small amounts of P (up to around 4 wt.% in the calcined catalyst) had a beneficial effect in the surface parameters and catalytic performance of this material, when compared to SARM in the hydrogenation of polyaromatic compounds, whereas higher amounts of P lead to sharp decreases in the surface area and hence poorer catalytic performance [13]. The material produced by this new activation method will be referred here as phosphorous-activated red mud (PARM), or sulfided-phosphorous-activated red mud (SPARM). The deactivation of these catalysts (SARM and SPARM) in the hydrodechlorination of TTCE has been studied in a recent work [14]. For these catalysts, an important enhancement of the resistance to HCl poisoning was observed, being the formation of carbonaceous deposits the main deactivation cause.

Concerning to the hydrotreatment catalysts (nickel-promoted molybdenum sulfide supported on γ-alumina is the most studied catalyst), it was observed that HCl poisoning is the most important deactivation cause [15].

The main objectives of this work have been to compare the performances of these RM based catalysts and a commercial hydrotreatment catalyst (Ni–Mo), and to study the kinetics of the hydrodechlorination reaction over the mentioned catalysts, developing a kinetic model to predict the catalytic behavior.

2. Experimental

2.1. Materials

The RM used in this work (19% Fe) was supplied by the San Ciprián (Lugo, Spain) plant of the Company Inespal-Alcoa. Details about composition, and morphological parameters are given in [9,10,12,13] and summarized in Table 1.

The commercial hydrotreatment catalyst tested was Shell S-214, a commercial nickel–molybdenum on γ-alumina hydroprocessing catalyst (2.8% NiO, 13.5% MoO_3, supported on γ-alumina). The catalyst is available as pellets, which were crushed to a particle size of 0.13–0.25 mm.

Table 1
Bulk composition and surface area of RM samples (wt.%)

Element	RM	ARM	PARM
Fe	19.7	25.1	23.6
Ti	13.0	16.1	14.5
Al	7.9	9.0	8.4
Na	3.7	0.1	0.0
Ca	5.1	0.9	2.0
Si	4.7	4.9	4.1
P	0.1	0.2	3.9
Surface area (BET, m^2/g)	24.3	82.4	80.4

2.2. RM activation

The method of Pratt and Christoverson for enhancing the catalytic activity of RM consists in dissolving the RM in aqueous HCl, boiling the resulting solution for 2 h, and producing a precipitate by addition of aqueous ammonia until pH = 8. The precipitate is then filtered, washed with distilled water, dried at 383 K overnight, and calcined in air at 773 K for 2 h [11]. The alternative activation method used in the present work consists in adding a mixture of aqueous HCl and H_3PO_4 to the solution obtained by dissolving the RM according to the method of Pratt and Christoverson. The ratio between the two acids was adjusted in order to get a 4 wt.% P in the calcined catalyst. The resulting precipitate is filtered, washed, dried and calcined following the previously described method.

2.3. Reaction studies

Reaction studies were carried out in a continuous fixed bed reactor, consisting of a 45 cm long, 9 mm internal diameter stainless steel cylinder placed inside a tubular electric furnace, and equipped with five thermocouples at different reactor lengths. Two grams of catalyst (crushed and sieved to 75–100 μm), previously dried at 110 °C and diluted with inert corundum were placed in the mid-section of the reactor, the lower and upper sections being filled with low area inert alumina (100–200 μm).

The liquid feed consisted of 10 wt.% TTCE dissolved in hexane, pumped downwards through the reactor by a liquid chromatography pump (Kontron LC). Hydrogen was fed co-currently, the flow rate being controlled by a mass-flow regulator. Reaction products were collected in a cylindrical receiver, connected to a back-pressure regulator that regulated the system pressure by venting the excess gas. A constant hydrogen flow of 0.8 Nl/min, corresponding to a minimum H_2/TTCE ratio of 20, was used in all the experiments.

Liquid samples were taken by emptying the receiver at selected time intervals. The equipment was provided with safety features such as redundant temperature control and a rupture disk. More details about the experimental set-up are given in [16].

Catalysts were sulfided in situ before use by passing 3 l/h of a mixture 10% H_2S–90% H_2 (vol.%) at 400 °C and atmospheric pressure through the reactor for 4 h. In most experiments, 1 wt.% carbon sulfide (which at reaction conditions is transformed to H_2S) was added to the liquid feed to maintain the catalyst in sulfided form. In previous studies with SRM it was observed that 1 wt.% is the optimal amount of CS_2 in the liquid feed in order to increase the stability of the catalyst, limiting the poisoning caused by H_2S [9,10].

The experimental conditions found to be optimal for this reaction [9] were hydrogen flow rate 0.8 l/min (at STP); temperature 350 °C and pressure 100 bar. A space time of 7.25 min g/mmol of TTCE was used in the preliminary and deactivation experiments.

Reaction products were analyzed by gas chromatography in a Hewlett-Packard 5890 apparatus equipped with an FID detector, using cycloheptane as internal standard and a 60 m × 0.53 mm internal diameter VOCOL fused-silica capillary column. The oven was maintained at 35 °C for an initial period of 15 min and then heated to 180 °C at 6 °C/min. Analyses were carried out in split mode. Peak assignment was performed by GC-mass spectra (Finnigan GCQ). Selectivities for ethane formation were higher than 99% in all the experiments carried out in this work. Only little amounts of trichloroethylene were found in the reaction products.

3. Results and discussion

3.1. Preliminary experiments: catalyst deactivation

Typical deactivation curves for the four studied catalysts are shown in Fig. 1. All these curves were

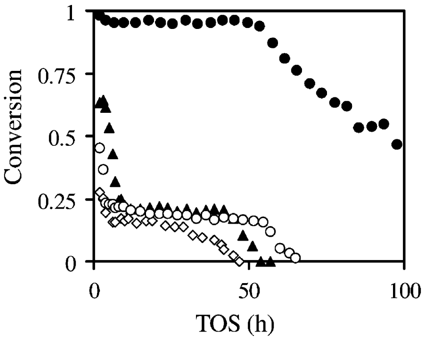

Fig. 1. Deactivation curves at 10 MPa and 350 °C for NiMo (●), SRM (◇), SARM (▲) and SPARM (○).

recorded at 350 °C, 10 MPa and 1% of CS_2 in the feed. It was observed that, although the commercial NiMo catalyst is more active, the resistance to the deactivation is very similar in the case of NiMo and SPARM catalysts. This aspect suggests that RM based catalysts could be an interesting alternative to the hydrotreatment catalyst since their price is much lower.

3.2. Kinetic experiments

Experiments were carried out in the constant catalytic activity period, at the following reaction conditions: 350 °C, 100 bar hydrogen pressure, hydrogen flow rate 0.8 Nl/min, and liquid flow rates between 0.3 and 3 ml/min, liquid flow rates being interspersed randomly during the experiments. Both gas-particle and intra-particle diffusion effects were negligible under the experimental conditions employed, according with the criteria of Carberry [20]. Moreover, plug flow behavior 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.

Conversions of TTCE as a function of space time are shown in Figs. 2 (SRM), 3 (SARM), 4 (SPARM) and 5 (NiMo). Comparison of results obtained in the presence and absence of carbon sulfide shows that the addition of CS_2 enhances the performances of SRM and SARM, whereas it has a very little effect on the performance of SPARM and the NiMo catalyst. The behavior of SRM and SARM, could be explained considering that, the primary catalytically active phase is pyrrhotite [10], a non-stoichiometric sulfide, which has a variable Fe/S stoichiometry depending on temperature and hydrogen sulfide partial pressure (an hence on the presence of carbon sulfide) [9–11]. In the case of SPARM, phosphorous is assumed to enhance the stability of the active phase [21], being less marked the effect of the operation parameters in the catalyst performance. Concerning to the hydrotreatment NiMo catalyst, two effects must be considered. On one hand, addition of CS_2 is a current practise in

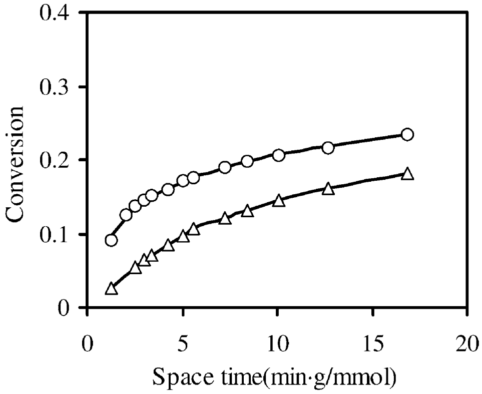

Fig. 2. Experimental conversion and calculated profiles for the catalytic hydrodechlorination of TTCE over SRM as a function of TTCE space time for a feed without CS_2 (△) and with 1% CS_2 (○).

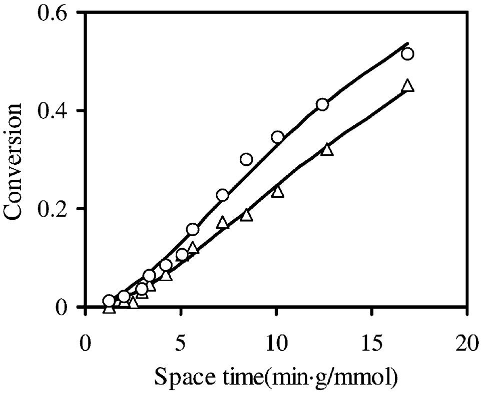

Fig. 3. Experimental conversion and calculated profiles for the catalytic hydrodechlorination of TTCE over SARM as a function of TTCE space time for a feed without CS_2 (△) and with 1% CS_2 (○).

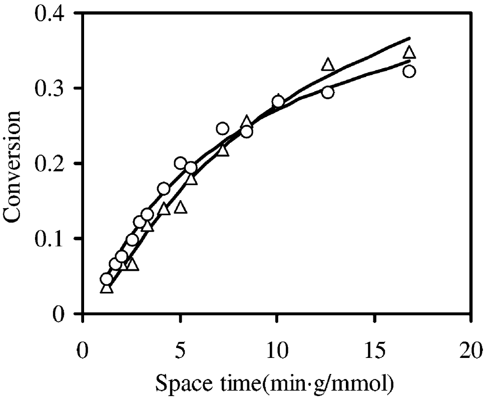

Fig. 4. Experimental conversion and calculated profiles for the catalytic hydrodechlorination of TTCE over SPARM as a function of TTCE space time for a feed without CS_2 (△) and with 1% CS_2 (○).

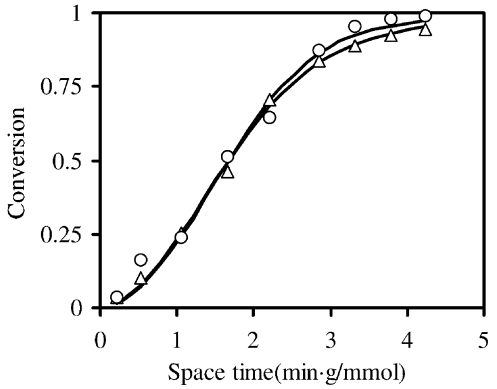

Fig. 5. Experimental conversion and calculated profiles for the catalytic hydrodechlorination of TTCE over sulfided NiMo catalyst as a function of TTCE space time for a feed without CS_2 (△) and with 1% CS_2 (○).

hydrotreatment reactions using these catalysts [17], however in the case of hydrodechlorination reaction, Hagh and Allen [22] state that the presence of H_2S (CS_2 is quantitatively transformed into H_2S at the reaction conditions) inhibits the hydrodechlorination over sulfided NiMo catalysts. In our case is observed that H_2S does not inhibit the reaction.

Concerning to the kinetic model, 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 [23]. Many kinetic models have been proposed for the hydrogenation of double bonds over sulfides [24], the most successful ones corresponding to the Langmuir–Hinshelwood type. Similar models have been used to model the kinetics of hydrodesulfurization and hydrodenitrogenation over sulfide catalysts [18,19,25], and for hydrodechlorination, (especially when organochlorinated molecules containing olefinic or aromatic structures are involved), over precious metals [26,27] and hydrotreating catalysts [28].

Adsorption of hydrogen is generally admitted to be dissociative over noble metal catalysts, but for sulfided catalysts there is debate about the nature of the adsorption, many authors considering it to be associative [24,25]. Other researchers consider the inhibition caused by the hydrogen chloride generated in the reaction, especially for catalysis by supported noble metals [29]. However, the interaction of hydrogen chloride with metal sulfides (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–Hinshelwood rate expression, in which only adsorption of TTCE and hydrogen (non-dissociative) is significant. These species are assumed to adsorb on the same active sites. The elementary steps involved in the reaction mechanism are the following:

$$\mathrm{TTCE} + \sigma \leftrightarrow \mathrm{TTCE}\text{-}\sigma \quad \text{(adsorption equilibrium for TTCE)} \qquad \text{(i)}$$

$$\mathrm{H_2} + \sigma \leftrightarrow \mathrm{H_2}\text{-}\sigma \quad \text{(adsorption equilibrium for } \mathrm{H_2}\text{)} \qquad \text{(ii)}$$

$$\mathrm{TTCE}\text{-}\sigma + \mathrm{H_2}\text{-}\sigma \rightarrow \mathrm{CCl_2H{-}CCl_2H}\text{-}\sigma + \sigma \quad \text{(rate controlling reaction)} \qquad \text{(iii)}$$

$$\mathrm{CCl_2HCCl_2H}\text{-}\sigma \rightarrow \mathrm{CCl_2{=}CHCl}\text{-}\sigma + \mathrm{HCl} \quad \text{(fast reaction)} \qquad \text{(iv)}$$

$$\mathrm{CCl_2{=}CHCl}\text{-}\sigma + 4\mathrm{H_2}\text{-}\sigma \rightarrow\rightarrow \mathrm{C_2H_6}\text{-}\sigma + 3\mathrm{HCl} \quad \text{(fast consecutive reactions)} \qquad \text{(v)}$$

$$\mathrm{C_2H_6}\text{-}\sigma \rightarrow \mathrm{C_2H_6} \quad \text{(desorption, fast)} \qquad \text{(vi)}$$

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

According to this model, the rate of disappearance of TTCE ($-r_{\mathrm{TTCE}}$, mmol TTCE/g-catalyst s) is

$$-r_{\mathrm{TTCE}} = \frac{kK_{\mathrm{TTCE}}K_{\mathrm{H_2}}p_{\mathrm{TTCE}}p_{\mathrm{H_2}}}{(1 + K_{\mathrm{TTCE}}p_{\mathrm{TTCE}} + K_{\mathrm{H_2}}p_{\mathrm{H_2}})^2} \qquad (1)$$

where “k” (mmol TTCE/g-catalyst s) is the intrinsic rate constant for the rate-controlling reaction, and “K_{TTCE}” and “$K_{\mathrm{H_2}}$” (MPa^{-1}) the adsorption equilibrium constants for TTCE and hydrogen, respectively.

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

$$\frac{\mathrm{d}x}{\mathrm{d}\tau} = -r_{\mathrm{TTCE}} \qquad (2)$$

Kinetic parameters were obtained by numerical integration of Eqs. (1) and (2) and the integrated equation

Table 2
Kinetic parameters for the hydrodechlorination of TTCE over sulfided NiMo catalyst (CC), SRM, SARM and SPARM in presence and absence of carbon sulfide

	CC		SRM		SARM		SPARM	
	Presence	Absence	Presence	Absence	Presence	Absence	Presence	Absence
k (mmol/g min)	1.72	1.645	1.3	0.15	0.161	0.129	0.198	0.154
K_A (MPa^{-1})	760	800	147	53.6	978.5	866.4	270.8	461.0
K_H (MPa^{-1})	9.8	7.9	1.6	9.1	6.7	4.4	14.7	12.5
r^2	0.995	0.996	0.995	0.997	0.994	0.997	0.997	0.997

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 phases are non-stoichiometric sulfides (specially in the case of iron sulfides), which has a variable metal/S stoichiometry depending on temperature and hydrogen sulfide partial pressure. 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 2. The good agreement between the experimental and calculated results can be observed in Figs. 2–5.

It is observed that SRM, the catalyst most sensitive to the CS_2 addition, presents the most important differences in the parameter values, being markedly lower the kinetic constant and the TTCE adsorption constant when CS_2 is not present in the reactor feed, whereas hydrogen adsorption constant is higher in this case. The differences between the parameters in presence/absence of CS_2 are less important for the other catalysts.

It is important to remark the different kinetic behavior of SARM (concave kinetic curve whereas SRM and SPARM present convex kinetic curves), although both behaviors are well represented by the proposed kinetic model. According to the results of the fit, the adsorption of H_2 is stronger in the SPARM, whereas the adsorption of TTCE is stronger in the case of SARM.

Alternative kinetic models were also considered. If the chemisorption of hydrogen sulfide (in the case of the experiment with CS_2 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 effect of H_2S was not considered, and the value of adsorption constants for H_2S were very closed to zero. If dissociative adsorption of hydrogen or hydrogen and TTCE adsorption on different active sites are considered, the fits of these models to the experimental results were of poorer quality. Models taking into account adsorption of hydrogen chloride, lead to inconsistent results and negative values of the kinetic parameters.

4. Conclusions

Sulfided RM is catalytically active for TTCE hydrodechlorination, although is less active than a commercial NiMo hydrotreatment catalyst.

The activity and stability of RM can be increased by simple activation procedures. The best results are obtained by activation in the presence of P.

The kinetics of the hydrodechlorination of TTCE over NiMo and RM derived catalysts can be modeled by a Langmuir–Hinshelwood mechanism, considering analogous active sites for the adsorption of H_2 (associative) and TTCE.

Acknowledgements

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