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Hydrodechlorination of 4-chlorophenol in water using Rh–Al pillared clays

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ABSTRACT

Catalytic hydrodechlorination (HDC) of 4-chlorophenol (4-CP) was studied using catalysts based on Al-pillared clays containing Rh. The Rh–Al pillared clays synthesized showed highly stable and no Rh leaching was detected. Two different hydrogen sources were used for this reaction with fairly different results. When using hydrogen gas, complete 4-CP removal was achieved even at mild operating conditions (25 °C, atmospheric pressure). The use of formic acid led to substantially lower conversion (65%) for equivalent reaction time, even when the reaction temperature was increased to 90 °C. The influence of Rh load and reaction temperature on the catalytic activity of Rh–Al pillared clays was checked. The stability of the catalyst was tested in repeated consecutive runs. A progressive increase of the catalytic activity was found up to the third reaction cycle due to the successive reduction of the metallic phase of the catalyst. After that, a decrease of activity was observed, probably due to the damage of the microporous structure.

1. Introduction

Nowadays the treatment of chlorinated organic wastes has become a major environmental concern. These compounds are commercially important chemicals, used as end products and intermediates in the manufacture of herbicides, dyes and plant growth regulators. They can be found among the most widely distributed pollutants in wastewaters and contaminated groundwaters being resistant to biodegradation [1,2]. Among the techniques proposed for their abatement, incineration can result in the formation of highly toxic by-products such as dioxins [2]. Therefore, alternate methods of treatment for these wastes that do not pose an environmental hazard must be developed. From a chemical point of view, oxidation or reduction methods can be employed for the removal of chlorinated organics.

Catalytic hydrodechlorination (HDC) can be considered as a potential environmentally friendly technique [3]. HDC has been applied to different types of chlorinated compounds such as polychlorinated benzenes, chlorophenols (CPs), PCBs, dioxins, etc., leading to their conversion into much less harmful species [4]. HDC includes advantages relative to the mild operating conditions of temperature and pressure allowing to achieve high conversions of CPs to harmless species with a low sensitivity to pollutants concentration [5–7].

The use of different reducing agents in hydrodechlorination has been described in the literature, being molecular hydrogen the most commonly employed. However, it shows different drawbacks for its application, above all in practical wastewater treatment such as its low solubility in water. Other possibilities that imply metal hydrides or other hydrogen sources such as formic acid and its salts, hydrazine or alkoxides, have also been used in this process [8–10]. Formic acid can be considered as a promising reducing agent although it has been scarcely studied. It is liquid at room temperature, which from an engineering point of view provides some advantages, and it is completely miscible with water, thus being possible its use in the treatment of wastewaters with a relatively high pollutants concentration. Few works can be found describing its use, although it has yielded satisfactory results in the hydrodechlorination of chlorobenzene using a Pd/Al_2O_3 catalyst [10]. Likewise, Pd supported on activated carbons [11] and Pd and Pt supported on Al pillared clays have been reported for the hydrodechlorination of 4-chlorophenol [12,13].

The HDC of chlorinated compounds in aqueous phase has usually been studied over supported metal catalysts. The most used active phases are based on metals such as Pd [5–7,10,14,15], Pt [16,17], Rh [16,18], Ru [4], Ni or Cu [15,19,20]. Bimetallic systems as Ru–Pd [21], Pd–Fe [22] or Pd–Rh [1,23] have also been studied.

The catalyst support plays an important role on both catalytic activity and stability. Although the effect of different supports in hydrodechlorination reactions has been extensively studied (activated carbon [4–6,24–26], alumina [2,16,27], Al-MCM-41 [28] or zeolites [29,30]), the knowledge on pillared clays (PILCs) as supports is still limited. The use of clays in heterogeneous catalysis is of interest for a number of reasons, being abundant natural materials. They are constituted by a two-dimensional network of interconnected micropores while the stacking of the clay lamellas creates mesopores, pillared clays possessing a bimodal pore structure [31].

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Table 1
Characterization of the starting materials and the Rh catalysts prepared.

Sample	Basal spacing d_{001} (nm)	BET surface area ($m^2\,g^{-1}$)	External area ($m^2\,g^{-1}$)	Micropore volume ($cm^3\,g^{-1}$)	Rh content (wt%)
Bentonite	0.98	35	24	0.005	–
Al-PILC	2.01	298	51	0.101	–
RhAl-IMP-0.5	1.92	205	36	0.089	0.54
RhAl-IMP-1	1.95	171	36	0.083	0.92
RhAl-IMP-2	1.95	168	40	0.079	2.05
RhAl-IMP-3	1.99	162	42	0.070	2.65
RhAl-IMP-5	1.95	156	57	0.048	5.10

Al-pillared clays have been used as supports of a great diversity of noble and transition metals and their use in different catalytic systems is extensively reported in the literature: Ni for hydrogenation of benzene [32], Pt for hydrogenation of adipic ester [33] or hydroconversion of heptane [34], Ru for hydrogenation of 1-butene [35], Ag for reduction of NO with NH_3 or C_2H_4 [36] and even bimetallic systems as Pd–Fe for dehalogenation of aryl halides [37].

In the present work, pillared clays with Rh–Al have been used as catalysts for HDC of 4-CP. To the best of our knowledge, this type of catalyst has not been used before for HDC. The literature reports the use of Rh–Al pillared clays for reduction processes both in liquid phase (hydrogenation of acetone [38] or quinoline [39]) and gaseous phase (hydrogenation of CO [40], selective catalytic reduction (SCR) of NO_x [41] and catalytic reduction of NO with CO [42,43]). The aforementioned applications suggest the potential of Rh–Al pillared clays as catalysts in reductive processes such as HDC for wastewater treatment. In this work the use of two reducing agents, formic acid and molecular hydrogen, has been tested. Moreover, the effect of reaction temperature and the stability of the catalyst have been studied. Finally, a simple kinetic model is proposed.

2. Materials and methods

2.1. Pillared clays preparation

The starting material used to prepare the pillared clays was a purified-grade bentonite supplied by Fisher Scientific Company. Al-PILC was prepared following the procedure described elsewhere [44] although in this case the final calcination temperature used was 350 °C.

The active phase, rhodium, was introduced into the Al-pillared clay structure by wet impregnation from a solution of $RhCl_3$ diluted in 0.2 M HCl. Catalysts with Rh loads amid 0.5 and 5 wt% were prepared. The set of catalysts prepared is summarized in Table 1. They are named as RhAl-IMP followed by the nominal Rh content. After impregnation, the wet solid was dried for 2 h at 25 °C, 14 h at 110 °C and calcined for 2 h at 500 °C.

2.2. Characterization methods

X-ray diffractograms of the pillared clays were obtained with a Siemens model D5000 diffractometer with CuKα radiation. To maximize the (0 0 1) reflection intensity, oriented clay-aggregate specimens were prepared by drying clay suspensions on glass slides. A Micromeritics Tristar 3000 apparatus was used to obtain the N_2 adsorption–desorption isotherms at 77 K. The samples were previously outgassed at 160 °C and 5×10^{-3} Torr for 16 h. Specific areas were obtained according to BET method. The metal content in the catalysts was measured by X-ray fluorescence with a TXRF EXTRA-II (Rich & Seifert, Germany) spectrometer after digestion of the samples by acid treatment (nitric, chlorhidric and sulphuric acids mixture) at 100 °C. Scanning electron microscopy (SEM) and energy-dispersive X-ray (EDX) microanalysis were carried out on a Philips XL30 microscope and EDAX DX4i equipment, respectively. The particle size distribution of the metallic phase was determined by transmission electron microscopy (TEM) using a JEOL 2100F microscope with a point resolution of 0.19 nm coupled with an energy-dispersive X-ray spectrometer (EDXS; INCA x-sight, Oxford Instruments) used for chemical elemental analysis. The carbon content was determined by elemental analysis with a LECO CHNS-932 apparatus. The TGA analyses were carried out in a Mettler Toledo TGA/SDTA851^e equipment.

2.3. HDC experiments

The hydrodechlorination experiments were carried out in jacketed stoppered glass reactors operating in batch, under continuous stirring. After stabilization of temperature, the corresponding amount of catalyst was added to 100 mL of an aqueous 4-CP solution (100 mg L^{-1}, i.e. 0.78 mol L^{-1}) and stirring was maintained for 15 min in order to allow 4-CP adsorption onto the catalyst (around 5 wt%). Next, either formic acid (liquid) or molecular hydrogen (gaseous), were fed to the reactor and this event was considered as the initial reaction time. Hydrogen was introduced by bubbling in the liquid reaction media with a continuous flow rate of 150 mL min^{-1}. Samples were withdrawn from the reaction medium at 15 min, 30 min and each hour until completing 4 h. In those experiments where the initial reaction rate was measured, samples were taken every 5 min for the first 15 min of reaction. The catalyst was separated by filtration using a nylon filter of 0.2 μm pore size. The pH of the starting 4-CP solution was around 6.3, whereas phenol, cyclohexanone and cyclohexanol solutions yielded pH values between 5.8 and 5.9. The pH value of the reaction media was measured along the HDC experiments. In the case of the runs conducted with molecular hydrogen, after 4 h of reaction the pH value decreased to around 4.3. The decrease in pH was due to the formation of HCl as a result of HDC. This trend was observed in all the experiments and no significant differences were found among different experiments. In the case of the runs where formic acid was used as hydrogen source, the starting pH of the reaction medium was 2.6 and it increased slightly to 2.8–3.1 during the experiments due to the consumption of formic acid.

The HDC process was followed from the evolution of the concentrations of 4-CP and phenol, which were measured by HPLC with a diode-array detector (Prostar, Varian) using a C_{18} as stationary phase (Valco Microsorb-MW 100-5 C_{18}) and a mixture of acetonitrile and water (1:1, v/v) as mobile phase. The other reaction products identified, cyclohexanone and cyclohexanol, were analyzed by means of a GC/FID (GC 3900 Varian) using a 30 m length × 0.25 mm i.d. capillary column (CP-Wax 52 CB, Varian) and nitrogen as carrier gas. Replicates of the reactions yielded raw data reproducibility better than ±5%. The repeatability of the analyses was ±3% in the case of HPLC and ±5% for GC/FID.

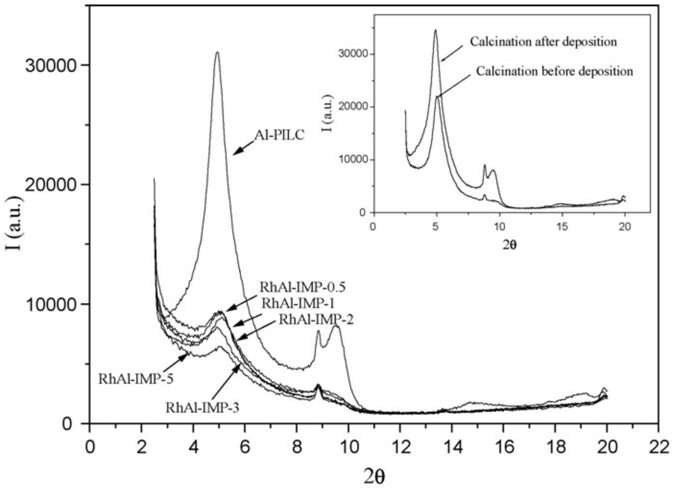

Fig. 1. X-ray diffractograms of the Al and Rh–Al pillared clays prepared. Inset: Al-pillared clay calcined at 350 °C before and after deposition on glass slides.

3. Results and discussion

3.1. Characterization of the pillared clays

The diffractograms of the Rh–Al pillared clays prepared are shown in Fig. 1. As can be seen the peaks corresponding to the (0 0 1) reflection are broader and with a lower intensity than that of the Al-PILC sample, also included in this figure, indicating a less uniform structure. Besides, the intensity of this peak decreased with increasing the Rh content in the pillared clay. Similar basal spacing values were obtained in all cases, since the maximum of the peak corresponding to the (0 0 1) reflection appears at almost the same 2θ angle value. On the other hand the peak around 9.5° in the Al-PILC diffractogram disappeared when Rh was introduced in the structure. This results from the way of preparing the samples for X-ray diffraction in each case rather than from the introduction of the precious metal in the pillared clay, as it is shown as an inset in Fig. 1. In this figure it can be seen that the second peak around 9.5° in the Al-PILC diffractogram disappeared when Rh was introduced in the pillared clay structure. This fact is due to the samples preparation procedure for X-ray diffraction in each case: to obtain the diffractogram of Al-PILC this sample was deposited on a glass slide before its calcination at 350 °C. This is the suitable method of preparing pillared clays samples for X-ray diffraction since the (0 0 1) plains remain oriented and the diffractogram obtained presents a higher quality. However, when Rh–Al pillared clays were prepared, they had to be first calcined in order to fix the noble metal to the pillared clay structure and next they had to be deposited on the glass slides after calcination. Comparing the effect of calcination of the Al-PILC before or after its deposition on the glass slides to obtain the oriented aggregates (inset in Fig. 1), it can be seen that the second peak around 9.5° disappeared in the case of the sample calcined before its deposition on the glass slide. So, the disappearance of this peak is due to the preparation method and not to the introduction of the noble metal in the pillared clay.

Table 1 collects the values of basal spacing $d(0\,0\,1)$, BET surface area, external or non-microporous area and micropore volume, together with the Rh load of the pillared clays prepared. The Al and Rh–Al pillared clays showed higher basal spacing and surface area values than the starting bentonite, indicating a successful pillaring process. The basal spacing values calculated for the Rh–Al samples were slightly lower than that of Al-PILC. The BET surface area of the Rh–Al pillared clays decreased as the Rh load increased being always lower than that measured for Al-PILC.

The SEM and TEM images of the Rh–Al pillared clays synthesized are shown in Fig. 2. The EDX analyses confirmed that the bright particles in the SEM micrographs are composed mainly of Rh. The TEM images show a fairly similar Rh particle size in the 1 and 2 wt% Rh catalysts.

3.2. HDC of 4-CP using Rh–Al pillared clays

The initial chlorine/Rh molar ratios used in this work were in the range of 1.6–14.8. Comparable values can be found in the literature for HDC of 4-CP with Rh supported on a variety of materials. Diaz et al. [16] worked at a ratio of 8.4 with a 0.5 wt% of Rh on Al_2O_3 catalyst. Bovkun et al. [1] used a bimetallic Pd–Rh catalyst and the Cl/(Rh + Pd) molar ratio was 15.4. Pozan and Boz [23] used Rh/C and Pd/Rh/C catalysts for HDC of 2,4-dichlorophenol (2,4-DCP) at significantly higher Cl/Rh molar ratios of 400–1250. With the same target compound Yuan and Keane [18] tested a Rh/C catalyst with a metal load of 5 wt% at Cl/Rh molar ratios of 156–2290, while Gómez-Quero et al. [45], using Pd/Al_2O_3 catalysts, worked at initial Cl/Pd molar ratios between 23 and 1728.

3.2.1. Formic acid as reducing agent

In a first set of experiments formic acid was used as hydrogen source and RhAl-IMP-5 was the catalyst chosen. The starting formic acid to 4-CP molar ratio was varied within the range of 10–75. That ratio showed a significant effect as can be seen in Fig. 3 although relatively poor results, far from complete dechlorination, were always obtained. 4-CP conversion values ranging amid 25% and 65% were reached, the highest one obtained for a value of this molar ratio of 50. In all cases phenol was found to be the only reaction product.

Increasing the Rh load of the catalysts increased 4-CP conversion, achieving no more than 65% at the highest Rh load tested (5 wt%), as can be seen in Fig. 4. In these experiments the catalyst was previously reduced for 2 h at 90 °C under H_2 atmosphere.

Table 2 collects the initial HDC rates with the catalysts with different Rh loads. As can be seen, the values fall within the range of 0.7–1.7 $\text{mmol}\,\text{min}^{-1}\,\text{g}_{\text{Rh}}{}^{-1}$, fairly lower than those obtained using hydrogen directly as will be seen later. It can be observed that these initial reaction rate values decreased as the Rh nominal content of the catalyst increased.

In previous works [12,13] catalysts also based on pillared clays whose active phase was Pt or Pd were tested in the hydrodechlorination of 4-CP, using formic acid as reducing agent under similar operating conditions as the ones here used. Catalysts based on Pd showed a higher activity allowing complete 4-CP conversion at mild operating conditions (catalyst with 1.5 wt% of Pd at 50 °C, atmospheric pressure, 1 $\text{g}\,\text{L}^{-1}$ catalyst concentration, FA/4-CP molar ratio: 500) while catalysts with Pt only yielded complete 4-CP conversion for a metal load of 5 wt%, 90 °C, atmospheric pressure, 1.5 $\text{g}\,\text{L}^{-1}$ catalyst concentration and a FA/4-CP molar ratio of 1000. When Pt catalysts were used, phenol was the only reaction product obtained, while with the Pd catalysts a higher hydrogenation of the aromatic molecule was achieved producing cyclohexanone at

Table 2
Initial reaction rates of 4-CP HDC with the catalysts with different Rh loads using formic acid (molar ratio FA/4-CP: 50) at 90 °C, 0.1 $\text{g}\,\text{L}^{-1}$ 4-CP initial concentration and 1 $\text{g}\,\text{L}^{-1}$ catalyst concentration.

Catalyst	k (min^{-1})	r^2	Initial rate ($\text{mmol}\,\text{min}^{-1}\,\text{g}_{\text{Rh}}{}^{-1}$)
RhAl-IMP-0.5	9.0×10^{-4}	0.98	1.7
RhAl-IMP-1	1.2×10^{-3}	0.98	1.3
RhAl-IMP-2	2.1×10^{-3}	0.99	1.0
RhAl-IMP-3	2.6×10^{-3}	0.99	1.0
RhAl-IMP-5	3.6×10^{-3}	0.99	0.7

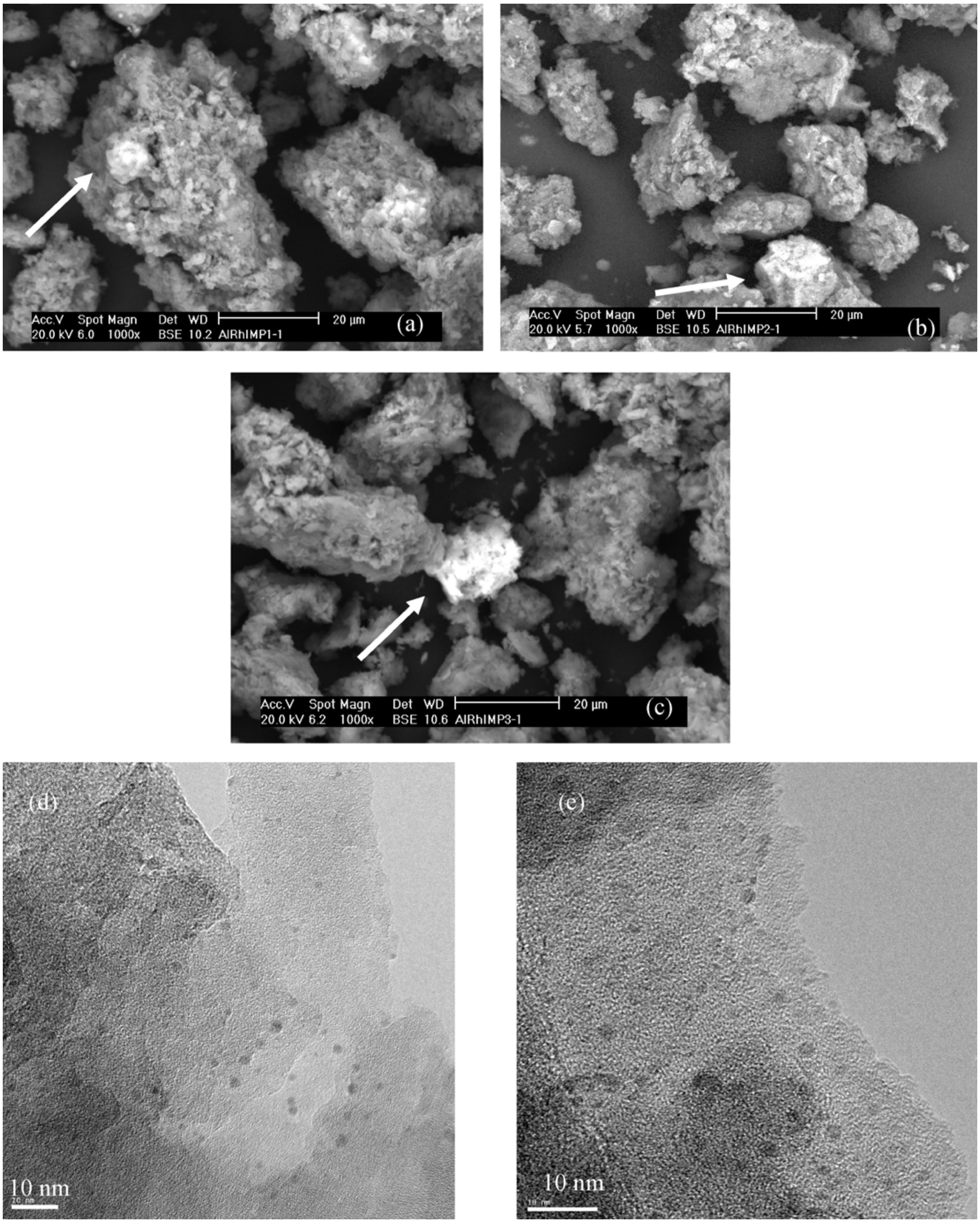

Fig. 2. SEM (a–c) and TEM (d and e) images of the Rh–Al pillared clays prepared: (a) RhAl-IMP-1, (b) RhAl-IMP-2, (c) RhAl-IMP-3, (d) RhAl-IMP-1 and (e) RhAl-IMP-2.

temperatures higher than 50 °C although the selectivity to cyclohexanone was fairly low.

On the other hand, Kopinke et al. [10] reported that a commercial catalyst 0.5 wt% Rh/Al_2O_3 was inactive for the HDC reaction of chlorobenzene using formic acid as reducing agent. In this work, with different catalyst support and target compound, some catalytic activity was found reaching a 4-CP conversion of 65% under certain operating conditions using also formic acid as reducing agent.

As a general conclusion, the results obtained using formic acid as hydrogen source for the HDC of 4-CP with these Rh–Al pillared clays show that even at fairly high Rh loads (up to 5 wt%) and a temperature of 90 °C this way would not provide an effective solution for the treatment of wastewaters containing this type of chlorinated pollutants.

3.2.2. Hydrogen as reducing agent

Fig. 5 shows the results obtained with the Rh–Al pillared clays at different Rh loads, using H_2. As can be seen, complete dechlorination was achieved in all cases in a relatively short reaction time, between 30 min and 1 h, depending on the Rh load. Further conversion of phenol into cyclohexanone and cyclohexanol was also complete in less than 2 h, except for the 0.5 wt% Rh catalyst, which required a higher reaction time. These results are much better than those obtained with formic acid as hydrogen source in spite of the fact that a lower temperature has been used now.

The shape of the curves in Fig. 5b suggests a series pathway where cyclohexanol is produced from cyclohexanone. In the case of the 0.5 wt% Rh catalyst, the cyclohexanone concentration did not peak within the 4 h of reaction time displayed in the figure due to the lower reaction rate. Hydrogenation up to cyclohexanol

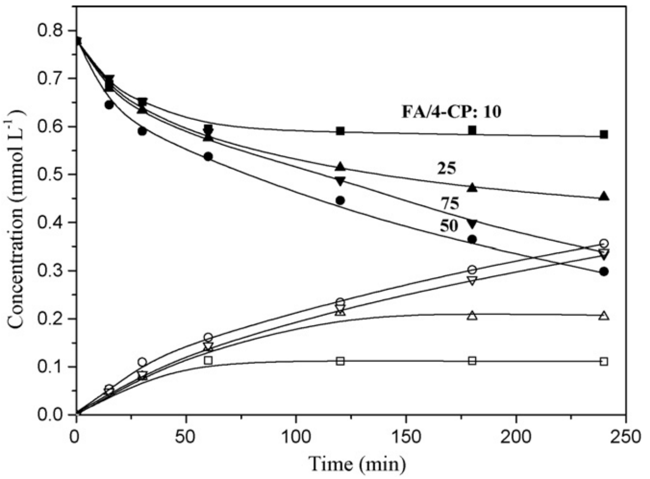

Fig. 3. HDC of 4-CP with RhAl-IMP-5 using formic acid (FA) as reducing agent at different molar ratios. Operating conditions: 90 °C, 0.78 mol L^{-1} initial 4-CP, and 1 g L^{-1} catalyst (solid symbols for 4-CP and open for phenol).

has some importance since the ecotoxicities of phenol and cyclohexanone measured by the Microtox test (EC_{50} values of 16 mg L^{-1} and 11.6 mg L^{-1}, respectively), are higher than the one corresponding to cyclohexanol (18.5 mg L^{-1}) [5]. These differences in toxicity are even more significant by the inhibition test (Daphnia magna), which yields LD_{50} values of 500 mg/kg for phenol, 1620 mg/kg for cyclohexanone and 2060 mg/kg for cyclohexanol [46].

Diaz et al. [16] did not achieve complete 4-CP dechlorination in the temperature range studied (20–40 °C) after 180 min of reaction with a catalyst Rh (0.5 wt%)/Al_2O_3 and the main product was cyclohexanone. Bovkun et al. [1], working with a combined silica sol–gel entrapped catalyst with Pd and Rh, obtained cyclohexane as the final product working at more severe conditions (120 °C, 27.6 bar of H_2). Likewise, Diaz et al. [16] reported a complete conversion of the phenol produced from 4-CP HDC using a semicontinuous basket stirred tank reactor at 40 °C and cyclohexanol was also obtained as reaction product but with a selectivity of no more than 25%. A reaction pathway is suggested in that work where besides phenol cyclohexanone was also produced from 4-CP dechlorination in a parallel reaction. Cyclohexanone is also produced from phenol hydrogenation. A similar reaction scheme seems to occur now with the Rh catalyst at a metal load of 1 wt% or higher but with the 0.5 wt% Rh catalyst cyclohexanone seems to be produced only from phenol since it appeared in the reaction media once the concentration of phenol started to decrease.

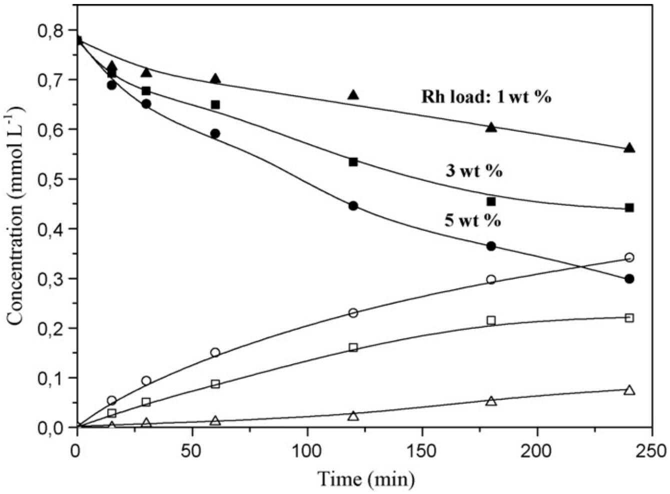

Fig. 4. HDC of 4-CP with Rh–Al pillared clays (1 g L^{-1}) of different Rh loads using formic acid (FA/4-CP molar ratio: 50) at 90 °C (solid symbols for 4-CP and open for phenol).

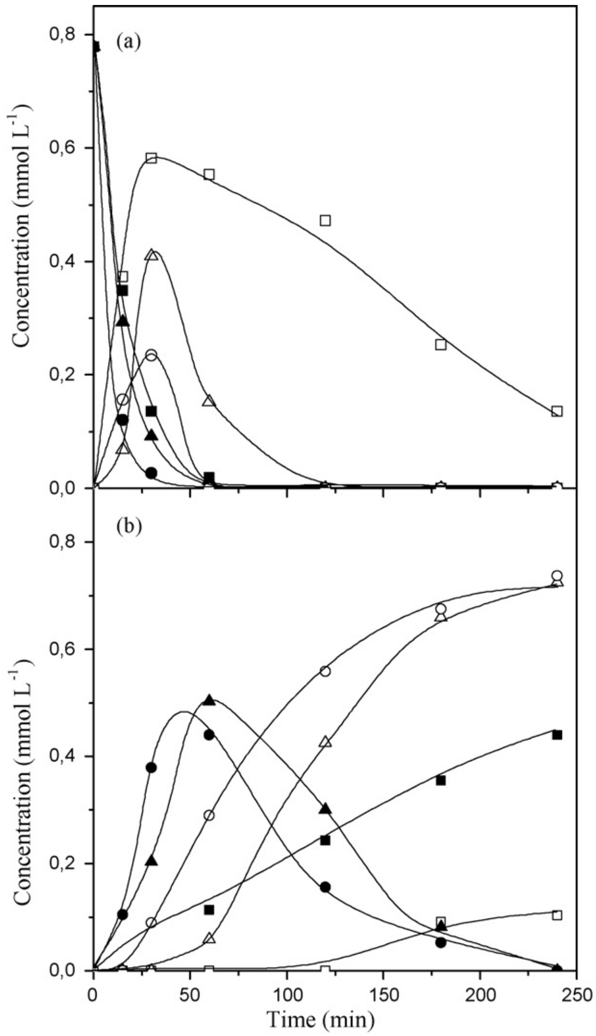

Fig. 5. HDC of 4-CP with Rh–Al pillared clays at different Rh loads (■, 0.5 wt%; ▲, 1 wt%; ●, 3 wt%) using H_2 (25 °C, 0.78 mol L^{-1} initial 4-CP, 1 g L^{-1} catalyst). (a) Solid symbols: 4-CP and open: phenol; (b) solid symbols: cyclohexanone and open: cyclohexanol.

In Fig. 6 the logarithm of 4-CP concentration is plotted versus reaction time and from the linear fittings the initial reaction rates were calculated. The good correlation supports a first-order kinetics for 4-CP HDC with these catalysts.

In Table 3 are collected the values of the initial reaction rates calculated from the fittings showed in Fig. 6. These values decreased when increasing the Rh load of the catalyst up to 2 wt%. Beyond that metal load a practically constant value around 40–45 mmol min^{-1} $g_{Rh}{}^{-1}$ was maintained, indicating that a higher

Table 3
Initial 4-CP HDC rates with the catalysts with different Rh loads using H_2 (25 °C, 0.1 g L^{-1} initial 4-CP, 1 g L^{-1} catalyst).

Catalyst	k (min^{-1})	r^2	Initial rate (mmol min^{-1} $g_{Rh}{}^{-1}$)
RhAl-IMP-0.5	6.3×10^{-2}	0.99	116.7
RhAl-IMP-1	6.8×10^{-2}	0.99	73.5
RhAl-IMP-2	8.9×10^{-2}	0.99	43.6
RhAl-IMP-3	11.3×10^{-2}	0.99	42.5
RhAl-IMP-5	23.1×10^{-2}	0.99	45.3

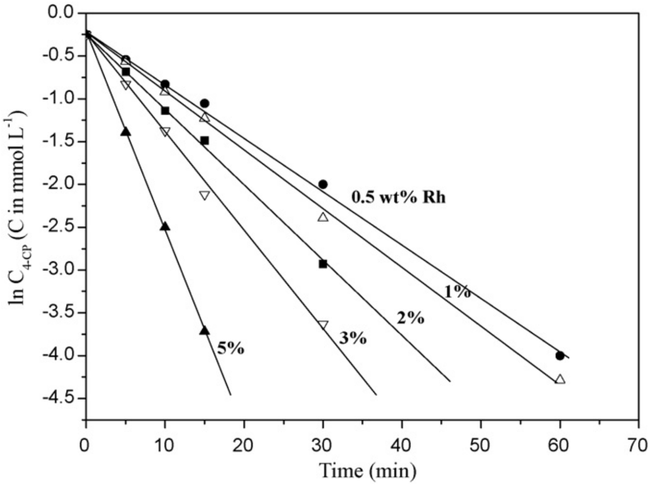

Fig. 6. First-order plots of 4-CP dechlorination with RhAl-PILCs with different Rh loads using H_2 (25 °C, 0.78 mol L^{-1} initial 4-CP, 1 g L^{-1} catalyst).

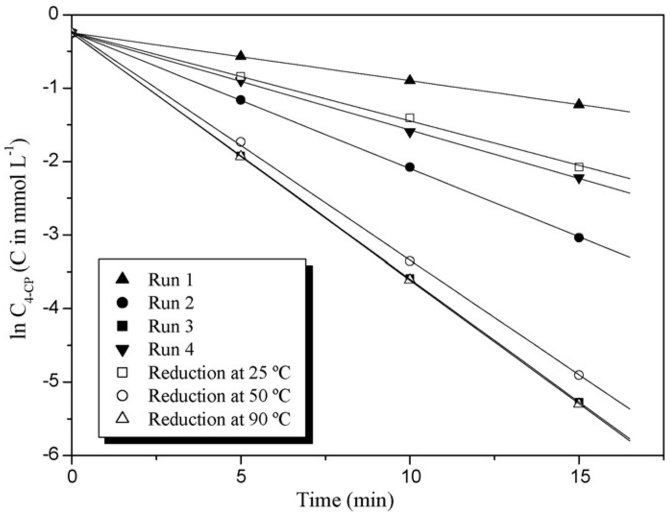

Fig. 7. First-order plots of 4-CP dechlorination with RhAl-IMP-1 and H_2 in successive runs (25 °C, 0.78 mol L^{-1} initial 4-CP, 1 g L^{-1} catalyst).

Table 4
Initial 4-CP HDC rates with RhAl-IMP-1 in successive runs.

Experiment	k (min^{-1})	r^2	Initial rate ($mmol\ min^{-1}\ {g_{Rh}}^{-1}$)
Run 1	6.8×10^{-2}	0.99	73.5
Run 2	18.6×10^{-2}	0.99	202.2
Run 3	33.5×10^{-2}	0.99	364.1
Run 4	13.2×10^{-2}	0.99	143.5
Reduction at 25 °C	12.1×10^{-2}	0.99	131.5
Reduction at 50 °C	31.2×10^{-2}	0.99	339.1
Reduction at 90 °C	33.6×10^{-2}	0.99	365.2

Rh load in the catalyst did not improve the specific activity. Diaz et al. [16] reported lower values (20.6 and 38.0 mmol min^{-1} ${g_{Rh}}^{-1}$ at temperatures of 20 and 40 °C, respectively) for the initial rate of 4-CP HDC using a Rh/Al_2O_3 (0.5 wt% Rh) catalyst. A higher value of 110 mmol min^{-1} ${g_{metal}}^{-1}$ has been reported by Yuan and Keane [18] with a 1 wt% Pd on activated carbon catalyst at 0 °C. The same authors reported much lower values for the initial reaction rate in the HDC of 2,4-DCP at the same reaction temperature of 0 °C using a 5 wt% Rh/C catalyst (6 mmol min^{-1} ${g_{metal}}^{-1}$) and a 1 wt% Pd/C catalyst (33 mmol $min^{-1}$${g_{metal}}^{-1}$). Pozan and Boz [23] reported also initial reaction rates for the HDC of 2,4-DCP: 45.3 μmol min^{-1} ${g_{cat}}^{-1}$ for a 0.80 wt% Pd/0.19 wt% Rh/C catalyst and 17.6 μmol min^{-1} ${g_{cat}}^{-1}$ for a 0.98 wt% Rh/C catalyst.

The apparent activation energy for the HDC of 4-CP was calculated by fitting to the Arrhenius equation the values of the first-order rate constant of 4-CP disappearance obtained at different reaction temperatures in the range of 25–50 °C. A value of 25.4 kJ/mol was obtained, comparable to the reported in the literature for other catalysts: 24.8 kJ/mol for Pd/AC [25], 41 kJ/mol for Ru/AC at 40–80 °C [4], 41.2 kJ/mol for Pd/C at 0–30 °C [18] and 47, 51 and 58 kJ/mol for Pd/Al_2O_3, Rh/AC and Pt/AC, respectively [47].

3.2.3. Catalyst stability

The RhAl-IMP-1 catalyst was checked in successive runs. After each run, the catalyst was separated by settling and the wetting liquid was removed under vacuum. After washing twice with deionised water and drying for 14 h at 110 °C, the catalyst was used again. Fig. 7 shows the logarithm of the 4-CP concentration versus reaction time of four successive runs. The corresponding initial reaction rates were calculated from these plots and the values are reported in Table 4. A progressive increase of the catalytic activity can be seen from the first to the third run, followed by a decrease in the fourth run.

Since the catalyst had not previously reduced this could explain the increase of catalytic activity from the first to the third HDC run. In order to confirm this hypothesis a fresh sample of RhAl-IMP-1 was submitted to reduction for 2 h under hydrogen flow (150 mL min^{-1}) at different temperatures: 25, 50 and 90 °C and then tested in 4-CP HDC. An increasing activity was observed as the reduction temperature increased from 25 to 90 °C (Fig. 7 and Table 4), that effect being more accused within the low temperature range. Likewise, the activity of the catalyst reduced at 90 °C for 2 h was similar to the one in the third HDC run (the highest observed).

The cause of the decrease in the catalytic activity after three successive uses cannot be attributed to the loss of the active phase by leaching, since Rh was never detected in the liquid phase after reaction. One possible reason for deactivation could be the formation of carboneous deposits on the catalyst surface which could partially block active centres. Elemental analyses of the catalyst after each HDC run showed an increase of the *C* content upon use reaching a maximum of 1.3 wt% after the third run (Table 5). The formation of carboneous deposits was also confirmed by TGA analyses. The *C* balances for the soluble species were matched with at least 92%.

The loss of activity could also be due to structural damages of the pillared clay upon use in successive HDC runs. To check this the X-ray diffractograms before and after each successive run were obtained (Fig. 8). There were no evidences of structural damage

Table 5
Textural properties and carbon content of RhAl-IMP-1 after successive HDC runs.

Sample	Basal spacing d_{001} (nm)	BET surface area ($m^2\ g^{-1}$)	External area ($m^2\ g^{-1}$)	Micropore volume ($cm^3\ g^{-1}$)	C (wt%)
RhAl-IMP-1	1.95	171	36	0.083	–
After 1st run	1.70	153	44	0.042	0.7
After 2nd run	1.63	146	48	0.040	0.6
After 3rd run	1.55	119	42	0.037	1.3
After 4th run	1.50	114	41	0.036	1.1

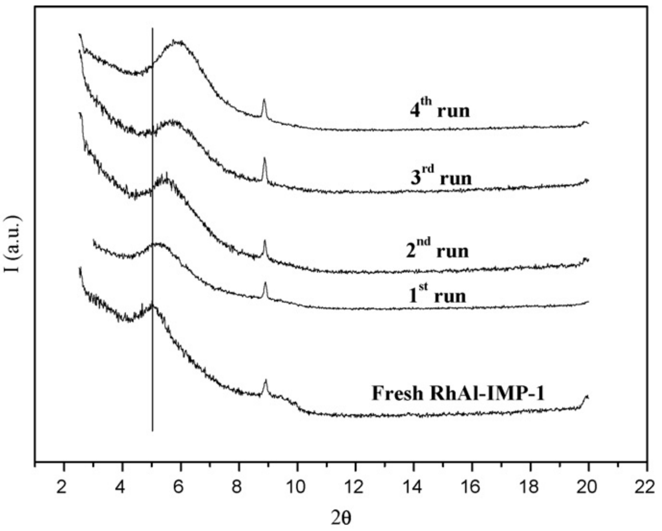

Fig. 8. X-ray diffractograms of RhAl-IMP-1 after successive HDC runs.

since the peak corresponding to the (0 0 1) reflection showed a high intensity, indicating a uniform pillared structure. However, this peak is progressively displaced towards higher 2θ values indicating a progressive decrease of the basal spacing (Table 5). This could limit the accessibility of reactants to the internal structure of the clay.

Finally, changes in the porous structure of the catalysts could also affect to the activity of the catalyst. The BET surface area decreased somewhat upon successive uses as can be seen in Table 5. That decrease affects essentially to the microporosity since the external or non-microporous area remained practically constant. The main change in the BET surface area occurred after the third HDC run being coincident with the highest value of *C* content analyzed on the catalyst.

4. Conclusions

Own-prepared Rh–Al pillared clays were tested as catalysts for the hydrodechlorination of 4-chlorophenol. Two different hydrogen sources, formic acid and hydrogen gas, were used, the second yielding substantially better results in spite of the lower temperature used. Complete 4-CP dechlorination was achieved at 25 °C and 0.5 wt% of Rh in the catalyst after 1 h of reaction time. Only phenol was detected as reaction product when formic acid was used as reducing agent while cyclohexanone and cyclohexanol, less toxic compounds, were generally the reaction products with H_2. A simple first-order rate equation described fairly well the intrinsic kinetics of the process. The apparent activation energy, 25.4 kJ/mol, was comparable to the reported with other catalysts for 4-CP HDC. The initial reaction rates were higher than the obtained in other studies using similar Rh loads in this reaction.

When the catalyst was used in successive runs an increase of the activity was observed from the first to the third run, probably due to the reduction of the metallic phase with H_2 since the preparation of the catalyst did not include a reduction step. Then, the catalytic activity decreased in the fourth run. No Rh leaching was observed. Likewise, the pillared structure was essentially preserved as confirmed by the X-ray diffractograms which showed the peak corresponding to the (0 0 1) reflection, even after four HDC runs. As possible causes of deactivation can be indicated a decrease of the BET surface area affecting to the microporous structure and the formation of carbonaceous deposits which could partially block active centres.

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