



Pd–Al pillared clays as catalysts for the hydrodechlorination of 4-chlorophenol in aqueous phase

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ARTICLE INFO

Article history:

Received 29 January 2009

Received in revised form 15 May 2009

Accepted 30 June 2009

Available online 5 July 2009

Keywords:

Pd–Al

Pillared clays

Hydrodechlorination

4-Chlorophenol

ABSTRACT

Catalysts based on pillared clays with Pd–Al were synthesized from a commercial bentonite and tested for catalytic hydrodechlorination (HDC) using 4-chlorophenol (4-CPhOH) as target compound and formic acid as hydrogen source. Stable Pd–Al pillared clays, with a strong fixation of the active phase to the solid support were obtained since no Pd was detected in the reaction media. The incorporation of Pd to the pillared clay structure yielded catalysts with high activity in the reaction studied reaching a complete removal of the 4-CPhOH under mild conditions of temperature (50–70 °C). Phenol was not the only reaction product formed, since a more hydrogenated product such as cyclohexanone was detected in the effluent, which indicates additional hydrogenation of phenol. The influence of the method of introduction of Pd in the pillared clay (ion-exchange or impregnation) and Pd concentration in the catalytic activity were studied as well as other important operating variables such as reaction temperature, catalyst concentration, 4-CPhOH initial concentration and formic acid to 4-CPhOH molar ratio. The catalysts prepared suffered deactivation after three consecutive runs, probably due to carbonaceous deposits formation since no appreciable Pd leaching was observed.

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1. Introduction

The catalytic hydrodechlorination (HDC) of chlorinated compounds has been a field of interest for the last years since this treatment can be considered as a viable, low cost and environmentally friendly method [1]. 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 substances [2]. They are usually used as versatile anti-microbial and disinfection agents as well as synthetic precursors for a variety of pharmaceuticals, glues, paints, dyestuffs and inks [3]. Owing to the recognition of CPs as toxic and hazardous to the environment [4], their production and application slowed down in recent years.

Though there are a number of processes and technologies available for the treatment of chlorinated compounds such as incineration, adsorption, biological treatment [5,6] or advanced oxidation processes [7,8], HDC is now emerging in the environmental field as a potential technique to treat these compounds. Besides, HDC shows advantages with respect to the aforementioned methods, including operation at low temperature and pressure, high conversion of CPs, no occurrence of more harmful side products, and low sensitivity to pollutants concentration [9–12].

The HDC of chlorinated compounds in aqueous phase has been reported over a variety of metal supported catalysts based on Pd [10–14], Pt [15,16], Rh [15,17], Ni or Cu [14,18,19]. From these studies, Pd appears to be the most active metal. The catalyst support also plays an important role on both catalytic activity and stability, owing mainly to the metal/support interactions. As consequence of these interactions, dispersion, size and morphology of the metallic particles are affected by the support. Although there is still a lack of comprehensive studies on the structure sensitiveness referred to HDC of CPs, it has been reported that smaller metallic particles exhibit higher specific activities, being alumina or activated carbon the supports used in the majority of the studies on HDC [20–23].

However, in the last two decades, the interest in pillared clays as catalysts has been increased due to their textural and catalytic properties in different reactions [24,25]. They constitute one of the new types of microporous materials used in heterogeneous catalysis. Aluminium is found to be among the most common cations used to build the pillars of the structure, yielding pillared clay materials with thermal and mechanical stability [26,27]. Pd–Al pillared clays have been previously described and tested their catalytic activity in reactions such as the hydrogenation of styrene and 1-octene [28], 1-phenyl-1-pentyne [29] and *n*-heptane [30] and selective catalytic reduction of NO with methane [31]. Also, Pd in combination with a promoter such as Cu introduced in pillared clays has been described as a highly active catalyst for nitrate conversion [32]. The above mentioned works show the potential of Pd–Al pillared clays as catalyst for reductive water treatment such as HDC. Besides

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the catalytic system, much of the success of the HDC depends on the reduction agent, being molecular hydrogen the choice in most of the studies. However, the use of a liquid reagent has some advantages, like easier dosage and handling. Some operating problems, as the high flammability of hydrogen, can be avoided as well. Besides, the low solubility of hydrogen in water can be a drawback regarding its application in water treatment. Thus, several hydrogen sources have been proposed for HDC reactions [33,34]. Formic acid can be considered as a promising reducing agent attending to both its properties and the results obtained in the hydrodechlorination of chlorobenzene using a Pd/Al₂O₃ catalyst [35] and in the hydrodechlorination of 4-chlorophenol with both Pd/AC [36] and Pt–Al pillared catalysts [37].

In this work, we study the activity of several Pd–Al pillared clays, prepared by two different methods (impregnation and ion-exchange) and with Pd contents between 0.5 and 5 wt% in the HDC of 4-chlorophenol in aqueous phase using formic acid as hydrogen source. Likewise, the effect of temperature, the 4-chlorophenol initial concentration and the formic acid to 4-chlorophenol molar ratio employed in the reaction were also investigated. Besides, a stability test was carried out in order to study the possible deactivation of the catalysts synthesized.

2. Material 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 (Loughborough, Oregon, USA). The chemical analysis (wt%) of this bentonite was: SiO₂, 52.22; Al₂O₃, 16.81; Fe₂O₃, 3.84; Na₂O, 1.26; MgO, 0.88; CaO, 0.74; K₂O, 0.80. The cation-exchange capacity (CEC) was 97 meq per 100 g of clay.

The Al–PILC was synthesized by intercalating the polyoxocations developed in a pillaring solution into the interlamellar galleries of the raw bentonite. This pillaring solution was prepared by slow addition of a 0.2 M NaOH solution to another 0.1 M AlCl₃ solution under constant stirring until an OH/Al molar ratio equal to 2 was reached. Afterwards, the oligomeric solution prepared was aged for 3 h at 90 °C and 2 h at 25 °C. Finally, the aged solution was slowly added to a 1 wt% suspension of bentonite in deionized water. A pillaring stoichiometry of 10 mmol Al per g of clay was used in this synthesis [38]. The exchange process was carried out at room temperature for 12 h under constant stirring. The resulting product was separated by centrifugation and washed with deionized water until chloride removal (conductivity lower than 10 μS). Air-drying of the clay was carried out at low temperature (60 °C). After air-drying, the intercalated clay obtained was submitted to calcination for 2 h at 350 °C.

Pd was introduced in the Al–PILC by two different methods: wet impregnation, a method reported to produce Pt–Al pillared clays [39,40] and wet ion-exchange, a method previously described in the literature to obtain Rh–Al pillared clays [41]. In this work, the content in Pd tested was within the 0.5–5 wt% range, which is the most commonly used in the literature [39,42–45].

Pd–Al pillared clays obtained by wet impregnation were prepared by the impregnation of the Al–PILC in powder form previously synthesized with a Pd solution of the desired concentration. This Pd solution was prepared by dissolving PdCl₂ in 0.1 M HCl (0.5 mL of solution per g of clay) due to the low solubility of this compound in water. After impregnation of the Al pillared clay with the Pd solution, the sample was subsequently subjected to drying at 25 °C for 2 h and at 60 °C for 14 h, followed by calcination at 500 °C for 2 h. Catalysts with a Pd nominal loading of 0.5, 1, 1.5, 2, 3 and 5 wt% were obtained and designated as PdAl-IMP-0.5, PdAl-IMP-1, PdAl-IMP-1.5, PdAl-IMP-2, PdAl-IMP-3 and PdAl-IMP-5, respectively.

The introduction of Pd in the Al pillared clay by ion-exchange was carried out from Pd solutions in HCl prepared as described previously. These solutions were diluted with water and mixed with the Al–PILC in order to obtain a volume for the exchange process of 20 mL per g of clay. Next, the mixture was stirred at 25 °C for 14 h. After the ion-exchange process, the pillared clay was separated by centrifugation and washed five times in order to eliminate the excess of Pd compound and other ions present. The washed product was dried at 60 °C for 14 h and calcined at 500 °C for 2 h. The Pd concentration in the exchanging solutions was adjusted in order to achieve the desired Pd load. The catalysts prepared with this procedure are next referred as PdAl-EXC-2, PdAl-EXC-3 and PdAl-EXC-5, respectively. Pd loads lower than 2 wt% were not used for ion-exchanged Pd–Al pillared clays because this method provides a lower incorporation of the noble metal in the pillared clay structure, as it has been proved in a previous work using Pt–Al pillared clays [37].

2.2. Characterization methods

X-ray diffractograms of the pillared clays were obtained with a Siemens model D5000 diffractometer using Cu K α radiation. To maximize the (001) reflection intensity, oriented clay-aggregate specimens were prepared by drying clay suspensions on glass slides. BET surface area values were determined from 77 K N₂ adsorption–desorption isotherms in a Micromeritics Tristar 3000 apparatus. The samples were previously outgassed at 160 °C under vacuum. The Pd content in the pillared clays synthesized was measured by means of the X-ray fluorescence technique with a TXRF EXTRA-II (Rich & Seifert, Germany) spectrometer after digestion of the samples by acid treatment at high temperature. Scanning electron microscopy (SEM) images 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 analysed by elemental analysis with an Elemental Analyzer LECO CHNS-932.

2.3. HDC experiments

The catalytic activity experiments for the hydrodechlorination of 4-CPhOH with the different Pd–Al pillared clays synthesized were performed in jacketed stoppered glass reactors operating in batch, under continuous stirring. After stabilization of temperature, the corresponding amount of pillared clay was added to 100 mL of an aqueous 4-CPhOH solution (100 mg L⁻¹) and it was stirred for 15 min allowing for 4-CPhOH adsorption onto the catalyst. Next, the amount of formic acid required to adjust the ratio of this reagent to 4-CPhOH used in each experiment was added to the reactor and this event was considered as the initial reaction time. Samples were withdrawn from the reaction medium at 15 min, 30 min and each hour until completing 4 h of reaction time. The catalyst in these samples was removed by filtration using a nylon filter of 0.2 μm pore size. Catalysts were used in powder form with a particle size lower than 100 μm. Taking into account the 4-CPhOH and catalyst concentration of each experiment, the values of the Cl/Pd molar ratio in this work were within the range of 1.8–19.3.

The HDC process was followed from the evolution of the concentration of the target reactant, 4-CPhOH, and the reaction products obtained (phenol and cyclohexanone). 4-CPhOH and phenol concentration values were measured by HPLC (ProStar, Varian) using a C₁₈ as stationary phase (Valco Microsorb-MW 100-5 C₁₈) and a mixture of acetonitrile and water (1:1, v/v) as mobile phase.

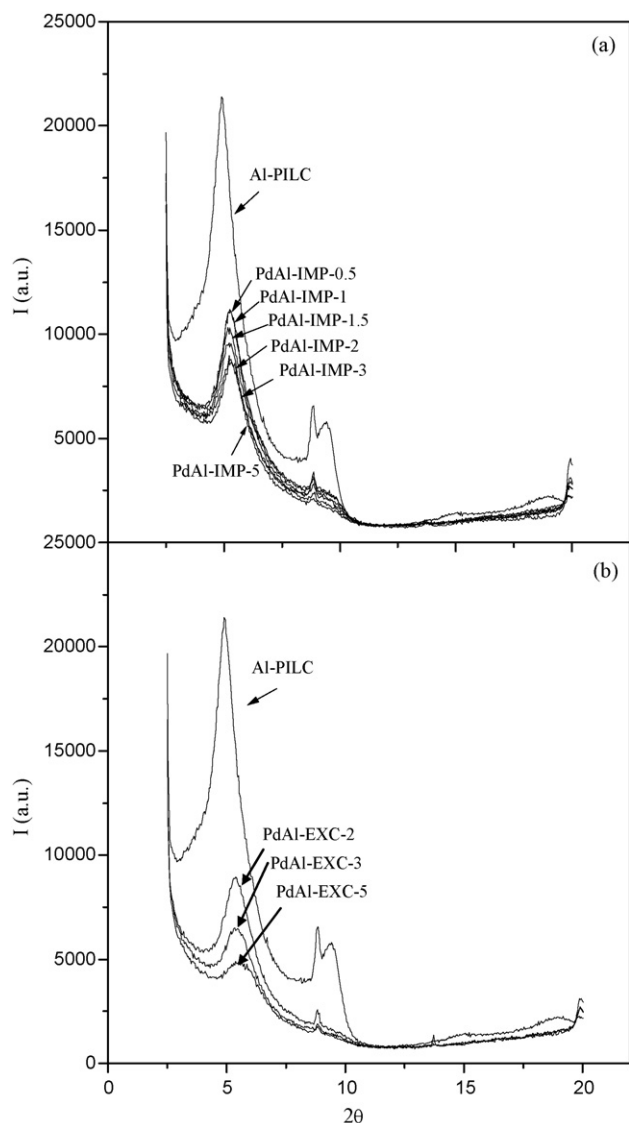


Fig. 1. X-ray diffractograms of Pd–Al pillared clays prepared by (a) impregnation and (b) ion-exchange.

Other possible products, i.e., cyclohexanone and cyclohexanol, were measured by means of a GC/FID (GC 3900 Varian) using a 30 m long \times 0.25 mm i.d. capillary column (CP-Wax 52 CB, Varian) and nitrogen as carrier gas. The raw data reproducibility calculated from triplicate tests using the same catalyst yielded values better than $\pm 5\%$. The analytical measurement repeatability was $\pm 3\%$ in the case of HPLC and $\pm 5\%$ for GC/FID.

3. Results and discussion

3.1. Characterization of the pillared clays

Fig. 1 shows the oriented powder X-ray diffractograms corresponding to the Al-PILC calcined at 350°C , base for the preparation of the Pd–Al pillared clays, whose diffractograms are also included. The Al-PILC exhibits a very sharp and intense peak corresponding to the (0 0 1) reflection, indicative of a fairly homogeneous development of the micropores throughout the pillared clay structure. The presence of a small second peak at 2θ around 9° , which corresponds to the main peak found in the pattern of raw Fisher bentonite, points out to the existence of a small fraction of un-pillared material.

In the case of the Pd–Al pillared clays prepared by impregnation (Fig. 1a), the peaks corresponding to the (0 0 1) reflection obtained are broader and their intensity is lower than that of the Al-PILC sample, indicating a less uniform structure. The diffractograms corresponding to the Pd–Al pillared clays prepared by ion-exchange (Fig. 1b) show (0 0 1) reflection peaks of lower intensity than Al-PILC sample and also than those obtained from impregnated pillared clays. In both cases a higher Pd load gave rise to a lower intensity of these peaks and a slightly higher width. However, the maximum of the peak corresponding to the (0 0 1) reflection remains practically at the same value of the 2θ angle, indicating a fairly similar basal spacing of the Pd–Al pillared clays prepared by the two methods.

Table 1 summarizes the values of basal spacing $d(001)$, surface area and Pd content of the pillared clays prepared in this work. The values corresponding to the starting bentonite are also included for comparison. The basal spacing values $d(001)$ were calculated from the Bragg's law using the value of the 2θ angle at which the maximum of the peak corresponding to the (0 0 1) reflection is obtained. It can be observed in this table that the pillaring process with Al with or without incorporation of Pd increased substantially the basal spacing respect to the starting bentonite. Besides, it can be seen that all the pillared clays synthesized by impregnation exhibit basal spacing values of about 1.86 nm, indicating a similar pore size for all of them. Pd–Al pillared clays obtained by the ion-exchange method gave rise to $d(001)$ values slightly lower than those of the samples prepared by impregnation, indicating a somewhat lower interlayer spacing.

The BET surface area values measured for Al-PILC and the Pd–Al pillared clays showed a significant increase respect to the raw bentonite, proving the success of the pillaring process. The Pd–Al pillared clays prepared by impregnation gave rise to surface area values around $180\text{ m}^2\text{ g}^{-1}$ for all of them, except for the samples with the highest Pd loads, PdAl-IMP-3 and PdAl-IMP-5, where the surface area decreased moderately. Ion-exchanged pillared clays showed higher surface area values, around $195\text{ m}^2\text{ g}^{-1}$ for the two samples with the lowest Pd loads and a slight decrease for the sample with the highest one. In all cases, the incorporation of a higher amount of Pd in the pillared clay structure led to a decrease in the surface area values. The decrease of BET surface area as Pd load increases can be due to a partial blockage of micropores. As can be seen in Table 1, the microporous area values decreased as the nominal Pd content increased and a slight decrease of the mesoporous volume within the 2–8 nm range was also observed.

With regard to the Pd content, measured by X-ray fluorescence, as can be seen, the theoretical and measured Pd loads of the impregnated samples are very similar, indicating that most of the Pd of the PdCl_2 solutions was retained in the pillared clay. However, this Pd incorporation was lower in the case of the ion-exchanged Pd–Al samples because when this preparation method is used, some metal could be removed from the pillared clay during the washing stage. The lower incorporation of Pd can explain in part the somewhat higher surface area. However, Pd incorporation is much higher than that obtained in a previous work when Pt was introduced in Al pillared clays by ion-exchange [37]. Analyses carried out by X-ray fluorescence showed the presence of residual Cl in the fresh catalysts, whose amount increased with the Pd load. This residual Cl can be attributed to the precursor (PdCl_2 in 0.1 M HCl). The percentage of Cl analysed in the catalysts varied from 0.01 to 0.18 wt% for Pd loads of 1.5 and 5 wt%, respectively. Anyway, this situation is common in the preparation of Pd catalysts from this precursor and in previous works no significant influence in the activity of the catalysts was detected [11,12,36].

The SEM images obtained for some of the Pd–Al pillared clays prepared are shown in Fig. 2. As can be seen, the sample prepared by impregnation (Fig. 2a) exhibit white particles of a considerable size. These white particles were analysed by EDX technique and it was

Table 1
Basal spacing, Pd content and porous structure of the pillared clays synthesized.

Sample	Basal spacing d_{001} (nm)	Surface area ($\text{m}^2 \text{g}^{-1}$)	Micropore area ($\text{m}^2 \text{g}^{-1}$)	Micropore volume ($\text{cm}^3 \text{g}^{-1}$)	Mesopore volume ($\text{cm}^3 \text{g}^{-1}$)	Pd content (wt%)
Bentonite	0.98	35	11	<0.01	–	–
Al-PILC	2.01	298	247	0.10	–	–
PdAl-IMP-0.5	1.86	189	148	0.10	0.02	0.43
PdAl-IMP-1	1.86	188	143	0.09	0.02	0.94
PdAl-IMP-1.5	1.88	187	138	0.08	0.02	1.46
PdAl-IMP-2	1.86	182	113	0.07	0.02	1.95
PdAl-IMP-3	1.86	146	82	0.05	0.01	2.85
PdAl-IMP-5	1.83	135	73	0.04	0.01	4.67
PdAl-EXC-2	1.83	198	110	0.05	0.02	1.73
PdAl-EXC-3	1.83	193	105	0.06	0.02	2.46
PdAl-EXC-5	1.78	179	81	0.05	0.02	3.99

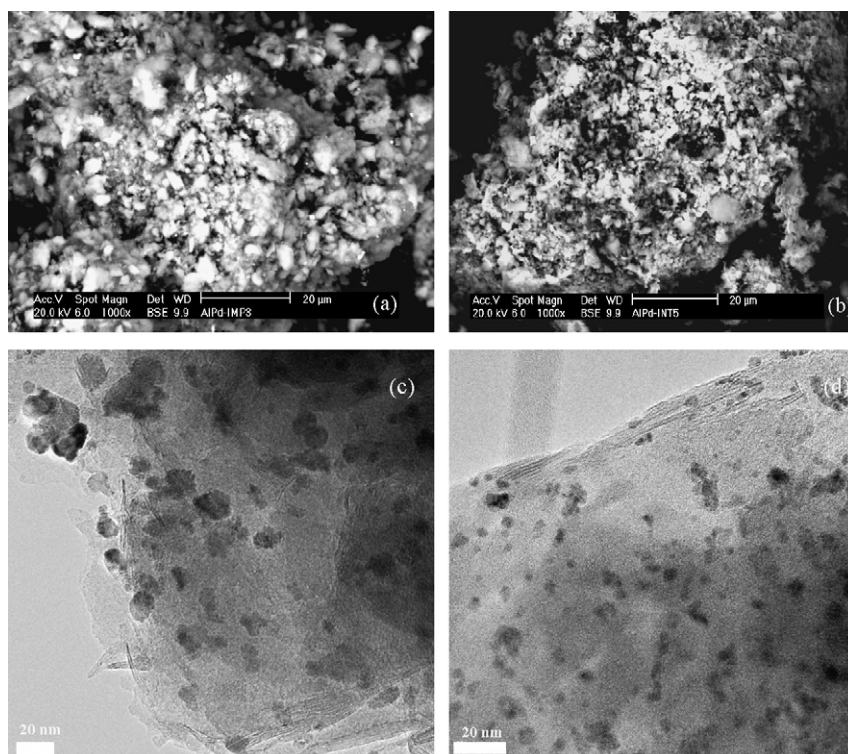


Fig. 2. Images of Pd–Al pillared clays prepared by impregnation and ion-exchange obtained by SEM: (a) PdAl-IMP-3, (b) PdAl-EXC-5 and TEM: (c) PdAl-IMP-1.5, (d) PdAl-EXC-2.

proved that they were composed primarily of Pd. Ion-exchanged pillared clays did not show large Pd particles, even for the sample with the highest Pd load PdAl-EXC-5 (Fig. 2b). This fact can be probably due to a higher dispersion of Pd in the internal structure. As a result of it, the blockage of pore mouths would be lower thus explaining the higher surface area showed by ion-exchanged pillared clays. TEM images confirmed this idea: as it can be seen in Fig. 2, the samples obtained by impregnation (Fig. 2c) gave rise to Pd particles with higher size (around 15–30 nm) than the ion-exchanged ones (Fig. 2d). In this last case most of the Pd particles showed sizes around 4–5 nm. In both cases a fairly homogeneous particle size distribution can be observed.

3.2. Activity of Pd–Al pillared clays in the HDC of 4-CPhOH

The activity of the Pd–Al pillared clays synthesized was studied in the HDC of 4-CPhOH using formic acid as reducing agent. Experiments carried out previously in the absence of catalyst and within the whole range of formic acid to 4-CPhOH molar ratio values proved that there is no homogeneous reaction between formic acid and 4-CPhOH [36]. The presence of a catalyst has also been

found to be essential for HDC of chlorophenols with molecular hydrogen [10]. Likewise, in the current case the catalyst is essential for the decomposition of formic acid to yield hydrogen [35]. During the reaction runs phenol was the main product identified and only cyclohexanone was obtained in some cases as a more hydrogenated product, although it must be taken into account that the CG/FID (technique used for measuring cyclohexanone and cyclohexanol concentrations) provides a detection limit of 3 mg L^{-1} . A dramatic decrease of ecotoxicity is expected, because the EC_{50} values for phenol, cyclohexanone and cyclohexanol are 16, 11.6 and 18.5 mg L^{-1} , respectively, while 4-CPhOH exhibits a much lower value of 1.9 mg L^{-1} [10,46].

3.2.1. Effect of the method of introducing Pd in the pillared clays

First, preliminary experiments were carried out in order to study the contribution of the adsorption of the species involved (4-CPhOH, phenol or cyclohexanone) using Pd–Al pillared clays prepared by impregnation (PdAl-IMP-1.5) and by ion-exchange (PdAl-EXC-5). These adsorption experiments were developed separately for each of the three compounds studied and in the absence of formic acid. As can be seen in Fig. 3 for PdAl-IMP-1.5, 4-CPhOH

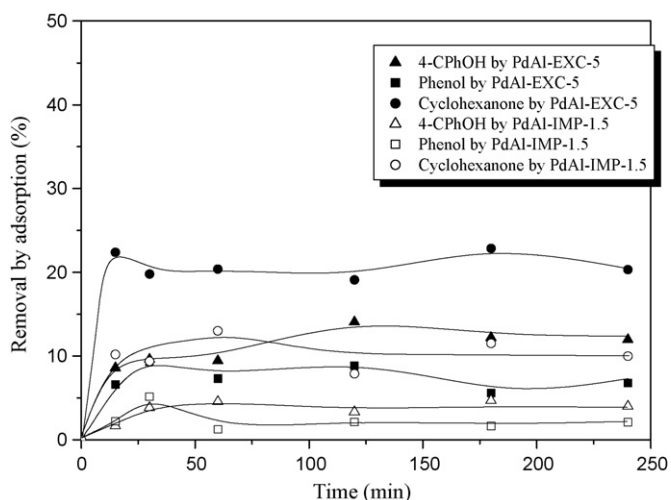


Fig. 3. Removal of 4-CPhOH, phenol and cyclohexanone by adsorption on PdAl-EXC-5 and PdAl-IMP-1.5. Initial concentration – 4-CPhOH: 100 mg L^{-1} , phenol: 100 mg L^{-1} , cyclohexanone: 50 mg L^{-1} .

and phenol were adsorbed in low extent, less than 5%, while cyclohexanone uptake was around 10%. When adsorption was studied on Pd–Al pillared clays prepared by ion-exchange, around 5% and 10% of 4-CPhOH and phenol were adsorbed, respectively, while cyclohexanone was adsorbed in the highest amount, around 20%, values all of them higher than the ones obtained for the impregnated samples.

Next, the effect of the Pd incorporation method on the activity of the catalysts was evaluated. Experiments of HDC of 4-CPhOH were carried out at 70°C using as catalysts the Pd–Al pillared clays containing 3 and 5 wt% of Pd. As can be seen in Fig. 4, Pd–Al pillared clays prepared by impregnation were more active for 4-CPhOH removal than those prepared by ion-exchange, reaching virtually complete 4-CPhOH conversion at reaction times as low as 15 min for the two catalysts prepared by impregnation. In the case of ion-exchanged Pd–Al pillared clays, a reaction time of 30 min and 1 h was needed with PdAl-EXC-5 and PdAl-EXC-3, respectively, to achieve complete 4-CPhOH removal. Phenol was detected as product in all cases, with a higher production in the case of the ion-exchanged catalysts.

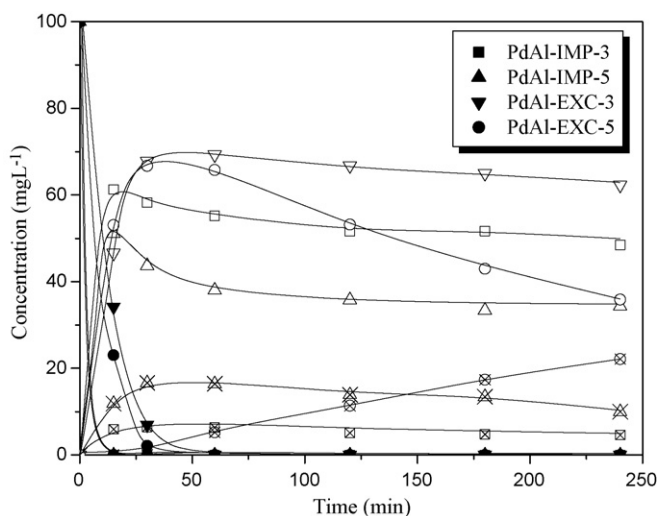


Fig. 4. HDC reaction of 4-CPhOH with Pd–Al pillared clays prepared by impregnation and ion-exchange at 70°C . Solid symbols for 4-CPhOH, open symbols for phenol, crossed symbols for cyclohexanone. Operating conditions – 100 mg L^{-1} of 4-CPhOH solution, 1000 mg L^{-1} of catalyst, formic acid to 4-CPhOH molar ratio: 500.

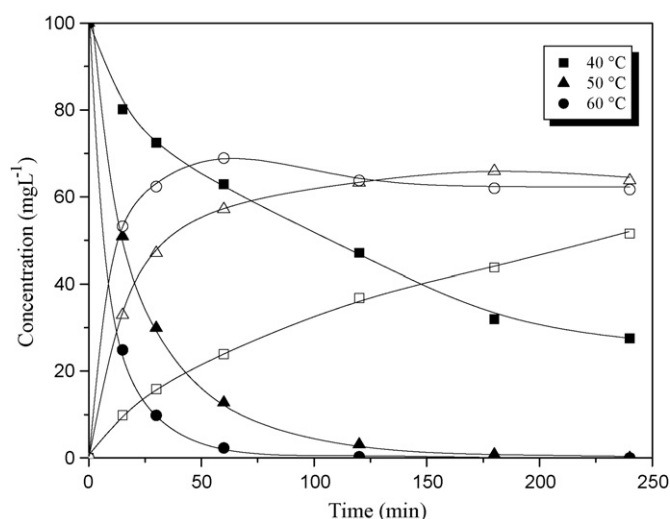


Fig. 5. Influence of temperature in the HDC of 4-CPhOH using PdAl-IMP-1.5. Solid symbols for 4-CPhOH, open symbols for phenol. Operating conditions – 100 mg L^{-1} of 4-CPhOH solution, 1000 mg L^{-1} of catalyst, formic acid to 4-CPhOH molar ratio: 500.

Both, impregnated and ion-exchanged Pd–Al pillared clays, show a decrease in the phenol concentration after 15 and 30 min of reaction, respectively, although in the case of PdAl-EXC-3 this decrease was very low. Cyclohexanone was also detected as product when impregnated samples and PdAl-EXC-5 were used as catalysts. In this last case a constant decrease in phenol production was observed together with a constant increase in cyclohexanone concentration, this being probably produced from phenol.

3.2.2. Effect of the reaction temperature

The effect of temperature in the HDC reaction of 4-CPhOH was tested for Pd–Al catalysts prepared by impregnation (Figs. 5 and 6) and PdAl-EXC-5 (Fig. 7). As can be seen in these three figures, temperature is a very important factor in this reaction, since a modest increase substantially improves 4-CPhOH conversion within the lowest temperature range tested (40 – 50°C). A further increase in reaction temperature up to 60°C shows a less pronounced effect (Fig. 5). From these results a temperature of 50°C was selected for the study of the following variables of reaction using Pd–Al pillared clays prepared by impregnation.

However, in order to find if a higher reaction temperature yielded reaction products other than phenol, some experiments were carried out with PdAl-IMP-1.5, PdAl-IMP-3 and PdAl-IMP-5 catalysts at 70°C (Fig. 6a) and 90°C (Fig. 6b). Only the catalysts with higher Pd loads, PdAl-IMP-3 and PdAl-IMP-5, produced cyclohexanone, with a decrease of phenol production in both cases, indicating that cyclohexanone could be produced from phenol. Fitting the values of the first-order rate constant of 4-CPhOH disappearance for the PdAl-IMP-1.5 catalyst to the Arrhenius equation a value of 85.8 kJ mol^{-1} was obtained for the apparent activation energy.

In the case of the Pd–Al pillared clays prepared by ion-exchange the effect of reaction temperature was investigated at the highest Pd load (PdAl-EXC-5), the results being shown in Fig. 7. As can be seen, the effect of temperature is dramatic in this case within the 50 – 70°C range, moving from a very low catalytic activity at 50°C to a rapid and almost complete 4-CPhOH conversion at 70°C . When temperature was raised up to 70°C , phenol concentration in the reaction media reached a maximum after 30 min of reaction and then, progressively, decreased until around 40 mg L^{-1} after 4 h or reaction. At 90°C phenol concentration increased until a maximum during the first 15 min of reaction and then decreased to

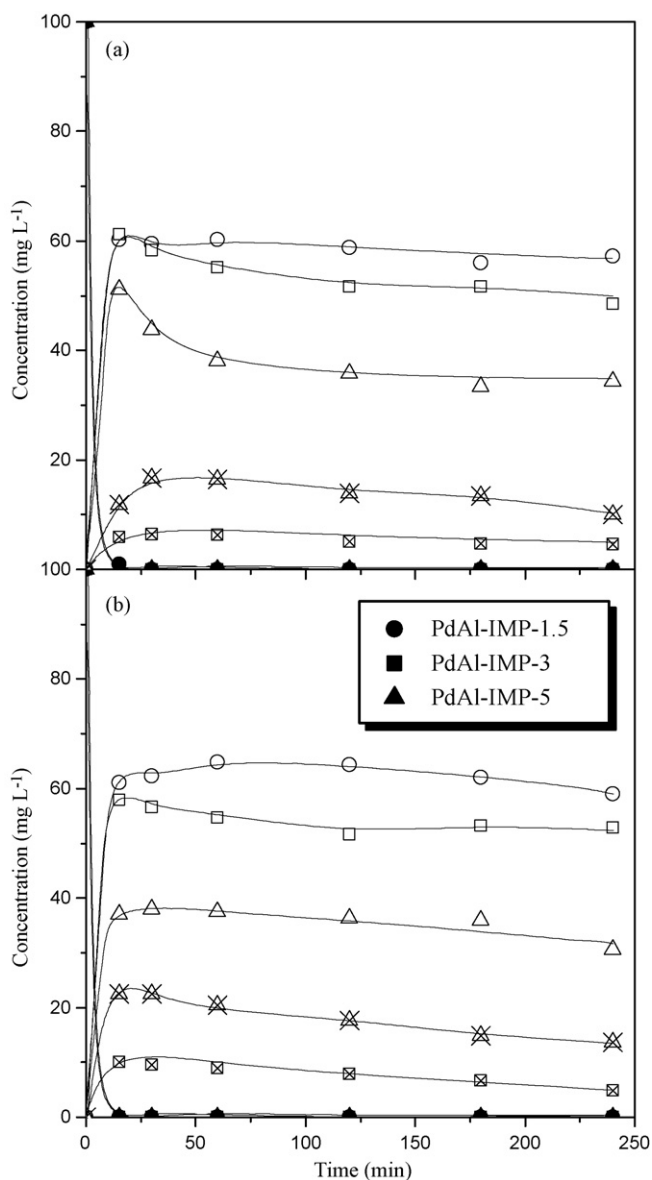


Fig. 6. Influence of temperature in Pd–Al pillared clays prepared by impregnation in the HDC of 4-CPhOH at (a) 70 °C, (b) 90 °C. Solid symbols for 4-CPhOH, open symbols for phenol, crossed symbols for cyclohexanone. Operating conditions – 100 mg L⁻¹ of 4-CPhOH solution, 1000 mg L⁻¹ of catalyst, formic acid to 4-CPhOH molar ratio: 500.

a constant value around 25 mg L⁻¹. Both at 70 and 90 °C, cyclohexanone was detected as product, appearing in the reaction media when phenol concentration started to decrease, confirming a chain mechanism where cyclohexanone is produced from phenol hydrogenation.

3.2.3. Effect of the Pd load

The effect of the Pd load for the Pd–Al pillared clays synthesized by the two methods, impregnation and ion-exchange, was studied. Taking into account the results previously discussed, different temperatures were used for each type of catalyst: 50 °C for the first ones (Fig. 8), 70 and 90 °C for the last ones (Fig. 9).

The plain Al-PILC provides a very low 4-CPhOH removal, around 10%, that could be attributed to adsorption. As can be seen in Fig. 8, the activity of the Pd–Al pillared clays catalysts prepared by impregnation increased with the Pd load, especially within the 0.5–1.5% range where a dramatic raise of 4-CPhOH conversion is observed.

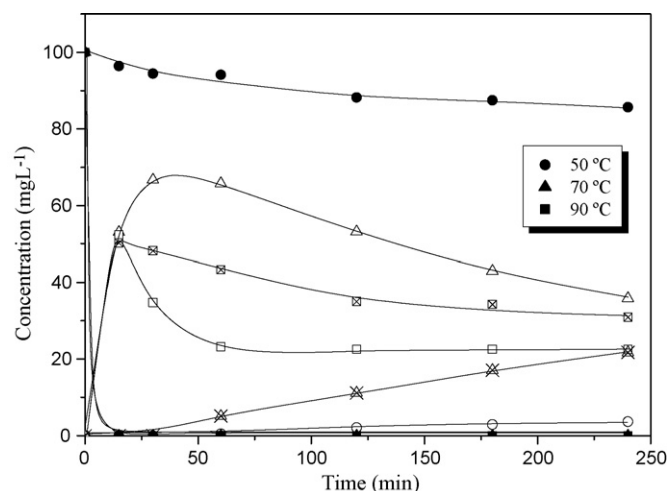


Fig. 7. Influence of temperature in the HDC of 4-CPhOH using PdAl-EXC-5. Solid symbols for 4-CPhOH, open symbols for phenol and crossed symbols for cyclohexanone. Operating conditions – 100 mg L⁻¹ of 4-CPhOH solution, 1000 mg L⁻¹ of catalyst, formic acid to 4-CPhOH molar ratio: 500.

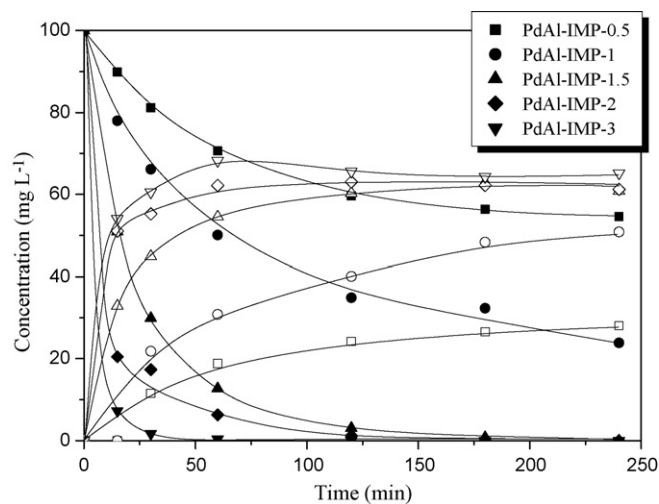


Fig. 8. HDC reaction at 50 °C of 4-CPhOH with Pd–Al pillared clays prepared by impregnation with different Pd loads. Solid symbols for 4-CPhOH, open symbols for phenol. Operating conditions – 100 mg L⁻¹ 4-CPhOH solution, 1000 mg L⁻¹ of catalyst, formic acid to 4-CPhOH molar ratio: 500.

Phenol was the only product detected in the reaction media at 50 °C and its production follows the same trend as 4-CPhOH conversion with respect to Pd load. From the 4-CPhOH and phenol concentration values, the mass balances were matched between 77% and 93%.

Initial reaction rates have been calculated for these catalysts (Table 2). As can be seen, the reaction rate increased with the Pd load up to about 3 wt% of Pd and then decreased for the catalyst with the highest Pd nominal content, which showed a lower surface area and a less microporous structure (Table 1). As a result of the higher Pd load higher size Pd particles could be formed which may partially block pore entrances limiting the accessibility to active centres.

As can be seen in Fig. 9a, the Pd load of the catalysts prepared by ion-exchange has a great effect on the catalytic activity at 70 °C, within the range of 2–3% nominal Pd content. Phenol production increased constantly in the case of PdAl-EXC-2, whereas in the cases of PdAl-EXC-3 and PdAl-EXC-5 the concentration of phenol reached a maximum after around 60 and 30 min, respectively, and then a steady decrease was observed. Cyclohexanone was detected only

Table 2
Initial rates of 4-CPhOH HDC using Pd–Al pillared clays prepared by impregnation with different Pd loads.

Sample	k (min ⁻¹)	r^2	Pd load (g)	Initial rate (mmol min ⁻¹ g _{Pd} ⁻¹)
PdAl-IMP-0.5	0.6×10^{-2}	0.99	4.3×10^{-4}	13.9
PdAl-IMP-1	1.1×10^{-2}	0.99	9.4×10^{-4}	11.7
PdAl-IMP-1.5	3.4×10^{-2}	0.99	14.6×10^{-4}	23.3
PdAl-IMP-2	10.6×10^{-2}	0.99	19.5×10^{-4}	54.4
PdAl-IMP-3	17.5×10^{-2}	0.99	28.5×10^{-4}	61.4
PdAl-IMP-5	18.4×10^{-2}	0.99	46.7×10^{-4}	39.4

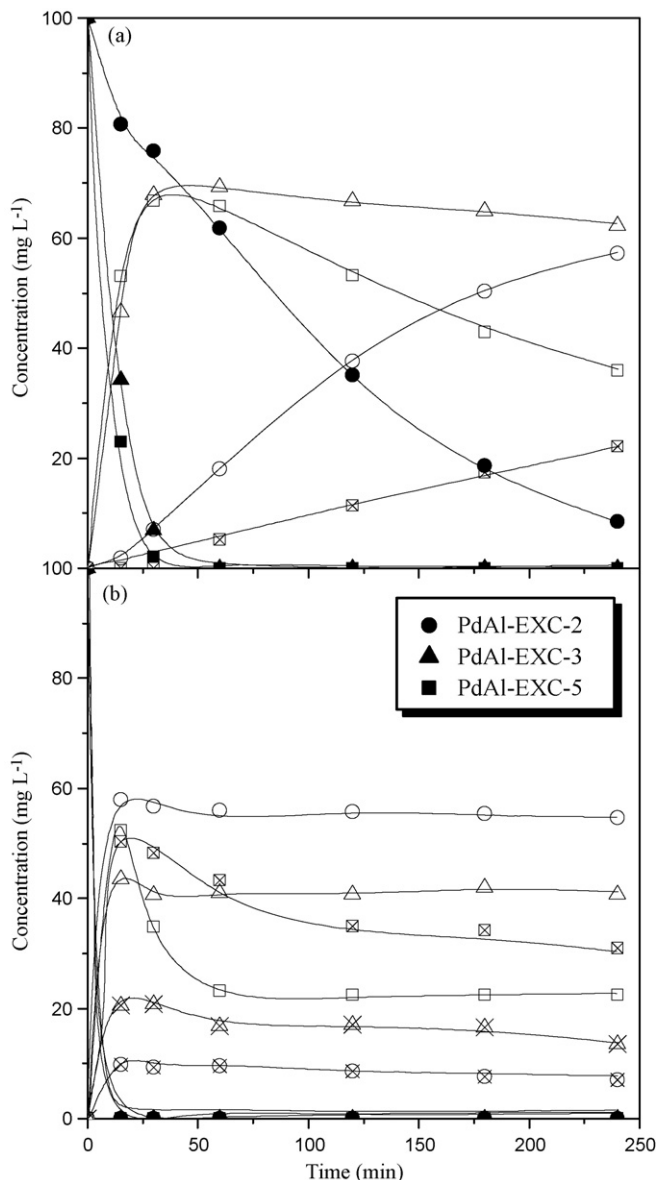


Fig. 9. HDC reaction of 4-CPhOH with Pd–Al pillared clays prepared by ion-exchange with different Pd loads and different reaction temperatures (a) 70 °C, (b) 90 °C. Solid symbols for 4-CPhOH, open symbols for phenol and crossed symbols for cyclohexanone. Operating conditions – 100 mg L⁻¹ of 4-CPhOH solution, 1000 mg L⁻¹ of catalyst, formic acid to 4-CPhOH molar ratio: 500.

for PdAl-EXC-5. At 90 °C (Fig. 9b) a very high 4-CPhOH conversion, close to 100%, was rapidly achieved at all Pd loads tested. The concentrations of phenol and cyclohexanone showed maxima and then decreased reaching steady values. This trend was more accused for phenol and with the highest Pd load catalyst. The decline in the concentration of cyclohexanone indicates its conversion to other reaction products not identified.

3.2.4. Effect of other reaction variables with PdAl-IMP-1.5

From the results so far, PdAl-IMP-1.5 was chosen to carry out the following experiments to analyse the influence of formic acid to 4-CPhOH molar ratio, catalyst concentration and 4-CPhOH initial concentration. The results obtained are collected in Table 3.

The effect of the formic acid to 4-CPhOH molar ratio was checked at three different values: 250, 500 and 750. As can be seen in Table 3, differences in 4-CPhOH conversion and phenol production were of low significance beyond a molar ratio of 500, being selected this value for the next experiments. Table 3 also shows the results obtained with different concentrations of the PdAl-IMP-1.5 catalyst between 500 and 1500 mg L⁻¹. As can be seen, within this range increasing the catalyst concentration leads to a higher 4-CPhOH conversion, with the important differences taking place mostly in the range up to about 1 g L⁻¹, being this value selected for analysing the HDC process at different 4-CPhOH starting concentrations, whose results are also presented in Table 3. Higher 4-CPhOH conversion values were achieved at lower starting concentrations of this target compound although at long reaction times the conversion achieved for initial concentrations of 50 and 100 mg L⁻¹ are equivalent and almost 100%.

3.2.5. Catalyst stability test

In order to check the stability of the catalysts based on Pd–Al pillared clays, PdAl-IMP-1.5 was submitted to three consecutive runs. After each run, the catalyst was separated by filtration, washed twice with deionized water and dried at 60 °C for 14 h. Fig. 10a shows the results obtained. As can be seen, non-expected results were found since the catalytic activity increased from the first to the second run and then a substantial decrease was observed in the third run. This behaviour was also observed for the PdAl-IMP-2 catalyst (Fig. 10b), which was tested in four consecutive runs. This increase of activity from the first to the second reaction cycle has been previously reported by other authors: Keane [4] observed the same phenomenon with a Pd catalyst supported on alumina for the hydrodechlorination of mono- and dichlorophenols using hydrogen. This was explained as the result of a beneficial restructuring of the catalyst over the first reaction cycle. Other authors found the same behaviour with Pt/Al₂O₃ catalysts in the hydrodechlorination of CCl₄ [47]. They submitted the catalyst to a pre-treatment with NH₄Cl which could serve to enhance the hydrogen-mediated dechlorination of CCl₄, effect that they attributed to metal particle restructuring.

To learn more in deep on this behaviour, the fresh catalyst PdAl-IMP-1.5 was submitted to a treatment reproducing reaction conditions, i.e., it was exposed for 4 h to formic acid at a concentration representative of that used in the HDC experiments and then it was washed twice with deionized water and dried overnight at 60 °C. As can be seen in Fig. 11, the activity of the catalyst submitted to this treatment increased but it did not provide the results obtained when the catalyst was submitted to a real HDC reaction.

With regard to the decrease of activity observed for both PdAl-IMP-1.5 and PdAl-IMP-2 after the second run (Fig. 10), it can not be explained by the loss of active phase by leaching. Pd was checked in the reaction media and in the water from catalyst washing between reaction cycles by means of X-ray fluorescence and its

Table 3
4-CPhOH conversion (%) at different operating conditions using the PdAl-IMP-1.5 catalyst at 50 °C.

Formic acid to 4-CPhOH molar ratio	Catalyst concentration (mg L ⁻¹)	4-CPhOH starting concentration (mg L ⁻¹)	Reaction time (h)		
			0.25	1	4
250	1000	100	34.7	69.9	98.4
500			41.1	87.3	100.0
750			50.4	83.4	98.8
500	500	100	28.6	65.5	89.4
	1000		41.1	87.3	100.0
	1500		66.4	97.8	100.0
500	1000	50	58.8	98.4	100.0
		100	49.1	87.3	100.0
		200	32.6	64.1	93.6

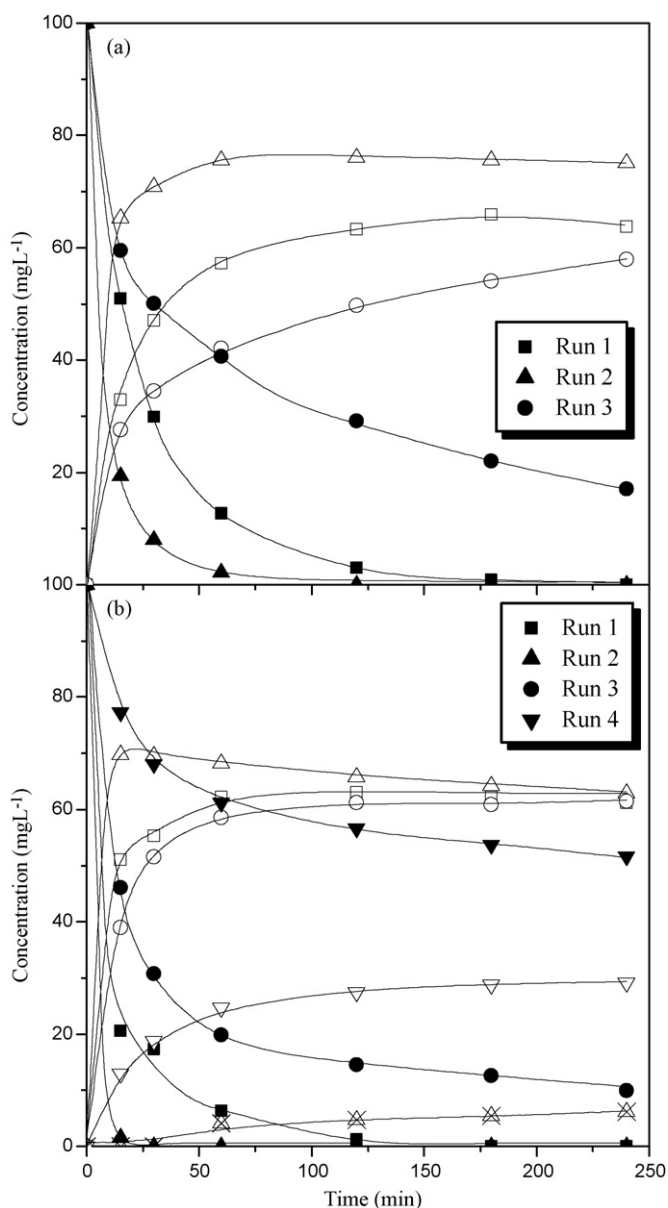


Fig. 10. Stability tests of (a) PdAl-IMP-1.5, (b) PdAl-IMP-2. Solid symbols for 4-CPhOH, open symbols for phenol, crossed symbols for cyclohexanone. Operating conditions – reaction temperature: 50 °C, 1000 mg L⁻¹ of catalyst concentration, 100 mg L⁻¹ of 4-CPhOH solution, formic acid to 4-CPhOH molar ratio: 500.

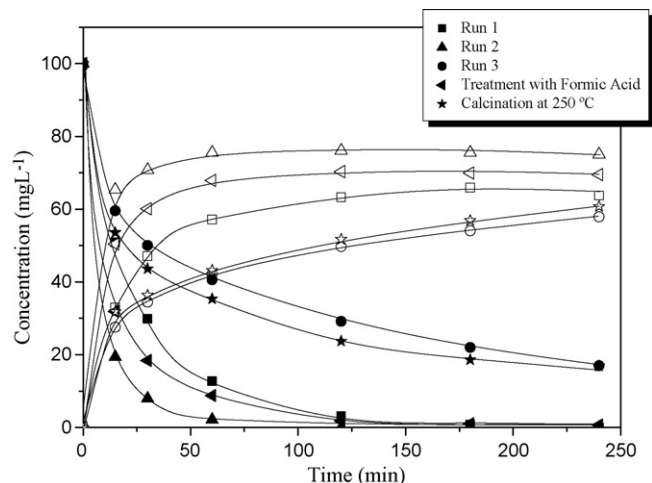


Fig. 11. Effect of the pretreatment with formic acid on the catalytic activity of PdAl-IMP-1.5 in the HDC of 4-CPhOH. Solid symbols for 4-CPhOH, open symbols for phenol. Operating conditions – reaction temperature: 50 °C, 1000 mg L⁻¹ of catalyst concentration, formic acid volume corresponding to a formic acid to 4-CPhOH molar ratio: 500.

concentration was in all cases below the detection limits (10^{-3} mg L⁻¹) of this technique. Besides, X-ray fluorescence analysis of the catalysts after reaction yielded percentages of Pd completely similar to the corresponding to the fresh catalyst, confirming the absence of Pd leaching.

Another possible cause for the catalyst deactivation could be the formation of carbonaceous deposits blocking active sites. Fresh catalysts, which are light grey coloured, turned to black after HDC experiments, which may be indicative of the formation of deposits. Elemental analyses of the catalyst before and after reaction proved the existence of these carbonaceous deposits. While fresh catalysts had a negligible C content, percentages around 1 wt% were analysed in the used ones. Besides, a significant decrease of BET surface area was observed, from 187 m² g⁻¹ measured for fresh PdAl-IMP-1.5 until 95 m² g⁻¹ for the catalyst used one time and 81 m² g⁻¹ after three consecutive runs. The carbonaceous deposits formed after the first run could modify the surface chemistry of the catalyst (this behaviour has not been observed in similar catalysts with Pt in a previous work), increasing its activity, while producing a partial blockage of the porous structure, suggesting some possible structural damages. After the second run, that blockage would be of importance, leading to a substantial decrease of activity.

Removal of these deposits could lead to the recovery of the catalytic activity. To check this, the catalyst used three times was calcined at 250 °C for 2 h. The resulting surface area (74 m² g⁻¹) was lower than the corresponding to the catalyst reused three times. On the other hand, as can be seen in Fig. 11, the catalytic activity was

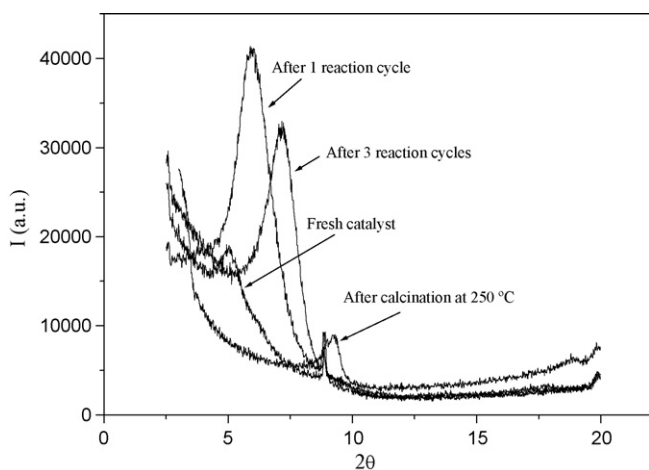


Fig. 12. X-ray diffractograms of PdAl-IMP-1.5 catalyst after successive reaction cycles.

slightly recovered with respect to the third reaction cycle but it was lower than the corresponding to the other reaction cycles. X-ray diffractograms from the catalysts after 1 and 3 reaction cycles are shown in Fig. 12 together with the corresponding to the fresh catalyst. As can be seen, the peak corresponding to (001) reflection moves toward higher 2θ angle values progressively upon use in successive cycles, indicating a decrease of basal spacing. This decrease is maybe related to the deposition of carboneous species on the walls of the pores. Fig. 12 shows also the X-ray diffractogram of the catalyst reused three times and then calcined at 250 °C. The (001) reflection peak is displaced to a higher 2θ angle value. Therefore, calcination did not cause an increase in the basal spacing in spite of a significant removal of the carboneous deposits as it was checked by elemental analyses. While the catalyst reused three times showed a C content of 0.82 wt%, this percentage decreased to a 0.33% upon calcination at 250 °C and about ten times when calcination was carried out at 500 °C. Nevertheless, the X-ray diffractogram obtained after calcination at this last temperature was very similar to the resulting upon calcination at 250 °C, indicating that the removal of carboneous deposits did not cause an increase of basal spacing. This fact could be probably due to structural damages suffered by the pillared clay upon calcination.

Carbon mass balances were performed for the different HDC experiments. Mass balance closures around 80–90% were most generally achieved when pillared clays prepared by impregnation were used as catalysts. Part of the unbalanced C may correspond to reactant and products adsorbed on the Pd–Al pillared clays. Nevertheless, desorption tests of the used catalyst with acetonitrile supplied almost negligible amounts of desorbed species in most cases.

An important amount of the unbalanced C could be attributed to the carboneous deposits on the catalyst surface, as it has been shown by the elemental analyses of the catalysts after reaction. These analyses yielded carbon contents between 1 and 3 wt% for the used catalysts. It was observed that carbon mass balance closures decreased at higher Pd loads and higher temperatures, that is, when the HDC reaction of 4-CPhOH proceeds in higher extension. In these cases, cyclohexanone was also found as product and, in some cases, even this product decreased its concentration. This could indicate the formation of other non-identified products or a lower formation of carboneous deposits from cyclohexanone. For Pd–Al pillared clays prepared by ion-exchange, the C mass balance closures showed similar trends than for the impregnated catalysts, although somewhat lower closure percentages were in general obtained.

In a previous work [37] a similar type of catalyst but using Pt instead of Pd was tested under the same conditions. For both metals the catalysts prepared by impregnation showed a higher activity than the ion-exchange ones. Pd showed always a higher activity than Pt although a similar poor behaviour was observed in both cases in terms of stability so that a rapid and important deactivation was observed. Metal leaching was negligible and thus can be excluded as a cause of deactivation, the formation of carboneous deposits being the most reliable explanation for that loss of activity.

4. Conclusions

Catalysts based on Pd–Al pillared clays have been synthesized and tested in the hydrodechlorination of 4-chlorophenol using formic acid as reducing agent at mild conditions. Two different methods, impregnation and ion-exchange, have been used for incorporating Pd into the pillared clay. The catalysts prepared by impregnation allow obtaining complete conversion of 4-CPhOH at low temperature (50 °C), while the ion-exchanged ones required higher reaction temperatures. Phenol was detected in all cases as the main reaction product while cyclohexanone was also produced when using Pd–Al pillared clays with high Pd loads and working at high temperatures (70–90 °C). The products distribution suggests that cyclohexanone is generated by hydrogenation of phenol, and not directly from 4-CPhOH.

The stability of these catalysts was analysed in three consecutive runs. An increase in the catalytic activity was observed from the first to the second reaction cycle. A possible explanation for this phenomenon could be the beneficial restructuring of the catalyst after the first run, as it has been pointed out by other authors. After that a gradual loss of activity was observed in successive runs. Pd leaching was negligible so that it can be excluded as a cause of deactivation. The formation of carboneous deposits seems to be most reliable explanation for the loss of activity. Elemental analyses of the used catalysts together with the C balances from the identified species support this conclusion. Research in course is addressed to elucidate the reaction mechanism and the phenomena causing catalyst deactivation.

Acknowledgment

The authors would like to thank the financial support from the Spanish Plan Nacional de I+D+i through the projects CTQ2005-02284 and CTQ2008-03988 and from CM-UAM through the project CCG08-UAM/AMB-4453.

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