



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

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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 Kα 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.

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