



Adipic ester hydrogenation catalyzed by platinum supported in alumina, titania and pillared clays

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ABSTRACT

Aluminum pillared clay (Al-PILC) and platinum impregnated pillared clay (Pt/Al-PILC) were prepared, characterized and tested as catalysts in adipic ester hydrogenation. Results were compared with those obtained for titania (TiO₂) and alumina (γ-Al₂O₃) as supports. Results indicate that platinum species are partially occupying the inner porous network of the pillared clay, a solid with an amphoteric character, and these crystallites are small enough to occupy the solid inner micropores. Alumina and Al-PILC supports are active as catalyst, allowing an adipate conversion of 26.3% and 83.3%, respectively, and the products distribution is very influenced by the solid surface acidity. When platinum containing catalysts were tested, the products distribution indicates that reactions of cracking and hydroisomerization, attributed to the acidity of the supports and to the presence of platinum, occur preferentially. However, the reduction in the acidity of Pt/Al-PILC, promoted by a barium bath, allowed the preparation of a catalyst more active and selective than the original catalyst, indicating that the acidity control step is crucial to the performance of this catalyst.

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1. Introduction

Catalytic processes are involved in large scale chemical compounds production and in fine chemistry. With the development of the petrochemical industry, oxidation and reduction catalytic processes have been widely used in the conversion of raw materials, such as olefins, alkanes, aromatics and esters, in functionalized derivatives of great commercial importance. However, in many of these processes, by-product formation occurs in greater amounts than the product of interest. This fact raises the costs considerably, besides disagreeing with the bulk of restrictions imposed for environmental protection [1]. Cases in which the reactional conditions are drastic are common. As example, we can cite the catalytic reduction of diesters and diacids to the respective diols. The 1,6-hexanediol is a valuable intermediary for the chemical industry. It has applications in the synthesis of some polymers and it is also used in fine chemistry. This linear diol contains two hydroxyl terminal groups. Such configuration results in a fast and simultaneous reaction for the formation of disubstituted products. The 1,6-hexanediol is used in the polyesters production for elastomers of

polyurethane, coverings, adhesives and plasticizers [2]. In addition, other products obtained from this catalytic reduction process have broad industrial application, among which caprolactone, used as raw material for the manufacture of thermoplastic polyester (mainly Nylon-6) and monomethyl ester of adipic acid, which are used as a lubricant and plasticizer in the manufacture of polyvinyl chloride.

Esters hydrogenation reaction is also called hydrogenolysis because, before the atomic hydrogen addition, rupture of one of the links C–O or O–R on the ester must take place. Thus, the selectivity reaction depends on the point where the hydrogenolysis occurs, with possible formation of many products such as alcohols (with diols among them), carboxylic acids, esters, lactones, cyclic ethers and hydrocarbons. Therefore, the development of a selective catalytic system is greatly attractive for the production of diol under less severe reactional conditions. Given the complexity of the esters and dicarboxylic acids reactions, the development of selective catalysts is essential and, in this context, the heterogeneous catalysis is a sufficiently promising alternative. Heterogeneous catalysts for reductions or oxidations in liquid phase can be obtained by immobilization of the active species in solid supports. This allows the recovery and recycling of these catalysts, besides preventing the formation of oligomers belonging to the oxo-metal species, normally inactive [3]. In the supports specific case, its superficial area, porosity, mechanical

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and chemical resistances are important in the reactional conditions. Considering these requirements, diverse inorganic materials can be used for catalysts preparation. In practice, only three have been used industrially: silica, alumina and coal [4].

More recently, various attempts have been made to develop catalysts from pillared smectite clays. Due to the small size of its particles ($<2 \mu\text{m}$) and to the high intercalation capacity, some clay minerals present high superficial area, useful in adsorption and catalysis processes [5]. Moreover, many specimens show catalytic properties, especially after having been submitted to small modifications in its composition or structure. Amongst the phyllosilicates, smectites are of special interest in the catalysts preparation. Smectites have structural layers separated by hydrated cation layers. Each structural layer is constituted by a central sheet of octahedral sites sandwiched between two sheets of tetrahedral sites, giving a 2:1 type of three sheet layer structures. In another main group of clay minerals, the ratio between octahedral and tetrahedral sheets is only 1:1, as observed for kaolinite [6]. Isomorphous substitutions for low valence cations confer negative charges to the structure, which must be balanced by exchangeable interlayer cations. Charges on the montmorillonite structure are originated by isomorphous substitutions both tetrahedral and octahedral sheets. Hydrated cations that compensate electric charges of the structure can easily be changed, conferring the smectites a higher capacity of ion exchange, differing in their structure from other phyllosilicates as mica, pyrophyllite and talc. Cation exchange capacity of montmorillonite varies between 80 and 100 meq for 100 g [7]. Moreover, the interlayer space can be expanded by adsorption of solvent molecules and many neutral species can be intercalated in the structure. The main properties of the smectites that favor their use in the preparation of pillared materials are related to their ease of expansion inside the interlayer spaces and to their relatively low charge density, fact that turns them compensation cations weakly attached to the structure [8]. Isomorphous substitutions in the smectite structure confer the possibility of generating Bronsted and Lewis acid sites on the surface. Bronsted acidity is related to silanol groups generated in the surface by rupture of siloxane bonds from tetrahedral sheets. Bronsted acidity is also formed from water molecules dissociation coordinated with cations (polarization effect) [9,10]. Aluminum(III) or magnesium(II) partially coordinated in the layers surface and charge compensation cations with acid characteristics confer the material Lewis acidity. By pillaring montmorillonite instead of saponite (a trioctahedral smectite), a less acidic catalyst support is obtained, since in saponites the negative layer charge is mainly due to tetrahedral silicon substitution for aluminum; thus the main source of acidity is attributed to aluminum neighboring silanol groups exposed at the surface. Therefore, acid sites originating from pillars are the main source of acidity in pillared montmorillonites.

Thermal stability, associated with the ease of access of reagent molecules into the interlayer catalytic sites, turn the use of pillared clays as increasingly attractive catalysts [11]. Compared with most oxides commonly used as supports, it is possible to regard pillars as responsible for some form selectivity in the reactions, since it is created a two-dimensional network of interconnected micropores. This paper exploits platinum as active metal, and TiO_2 , Al_2O_3 and aluminum pillared clay as supports. Catalysts were obtained with the impregnation method, not only because of its simple handling properties in the preparation process, but also due to the excellent performance presented by catalysts previously prepared with this method [12].

2. Experimental

2.1. Catalysts preparation

Catalysts were prepared by the impregnation method in aqueous suspensions, in order to obtain a solid with nominal concentration of 2% in platinum weight. Supports applied here were TiO_2 (titania, Aldrich, 99+%, crushed and strained in average fraction of 0.045 mm), $\gamma\text{-Al}_2\text{O}_3$ (alumina, Degussa type 213, crushed and strained in average fraction of 0.045 mm) and montmorillonite aluminum pillared clay (Al-PILC, Fluka). Precursor salt used was $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot 0.68\text{H}_2\text{O}$ (Aldrich, 98%). Impregnation was done by adding support and solution containing metallic precursor in a rotative evaporator, with bath at 333 K and vacuum for 5 h. Next, samples were oven dried for 12 h, at a temperature of 393 K. Catalysts were then subjected to calcination treatment for 4 h at 673 K, under 50 mL min^{-1} of synthetic air flow, and reduction for 2 h at 673 K, under flow of 40 mL min^{-1} of 2% H_2 and 98% N_2 mixture.

These catalysts were submitted to an impregnation with barium (Pt-Ba/TiO_2 , $\text{Pt-Ba/Al}_2\text{O}_3$ and Pt-Ba/Al-PILC), aiming to reduce the surface acidity. Each 2 g of catalyst were treated with 200 mL of 0.1 mol L^{-1} $\text{Ba}(\text{NO}_3)_2$. The system was kept under magnetic stirring at room temperature for 2 h. Solid phase was separated by vacuum filtration and washed with deionized water until absence of barium cations. This solid was oven dried at 383 K for 6 h and submitted to calcination and reduction treatments.

2.2. Characterization

A Micromeritics ASAP 2010 device was used to obtain adsorption-desorption measurements at 77 K, under pressure ranging from 10 to 925 mmHg. Before each measurement the samples were outgassed at 423 K and 1.3×10^{-3} Pa for 12 h. Specific areas were obtained according to Brunauer, Emmett and Teller (BET) method. The t -plot method was used to evaluate the micropore volume.

Diffraction patterns were obtained in a Shimadzu model XD-3A diffractometer, with $\text{Cu K}\alpha$ radiation. Spectra were registered between $2\theta = 2^\circ$ and 40° , with scanning speed of $2^\circ \theta \text{ min}^{-1}$, using a cathode current of 25 mA and a voltage of 35 kV.

Assays of temperature programmed reduction (TPR) were held on a quartz reactor, using 100 mg of each catalyst under flow of reductive gas mixture containing 1% hydrogen and 99% helium, at outflow of 25 mL min^{-1} . Analysis temperature was programmed to vary from 298 to 1073 K, with heating rate of 5 K min^{-1} . Throughout the analysis, hydrogen consumption profiles in function of the temperature were recorded by using a Balzers Omnistar Quadrupole Mass Spectrometer, model QMS200.

Hydrogen sorption was done with samples of 0.4 g of the catalysts. Initially, their surfaces were cleaned by evacuation of the system under flow of He at 393 K. After that, the catalysts was reduced "in situ" at 673 K for 2 h under flow of H_2 and the system was then evacuated under flow of H_2 for 1 h until reaching the sorption temperature (308 K). The sorption measurements were carried out under H_2 pressure varying from 10 to 400 mmHg.

Acid-base character of pillared clays was done by titration of their aqueous suspension with 0.1 mol L^{-1} HCl. Initial pH was adjusted to 9.0 by addition of 0.1 mol L^{-1} NaOH and pH at equilibrium was measured after subsequent addition of $0.05 \text{ mL } 0.1 \text{ mol L}^{-1}$ HCl aliquots, until reaching pH 3.0.

FTIR spectra of chemisorbed pyridine were obtained using a Nicolet Protégé 460 FTIR spectrometer. Each 10 mg sample was pressed (for 15 min at 10 ton cm^{-2}) into a self-supporting wafer of diameter 12 mm. The wafers were calcined in air at 773 K for 2 h

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