

Dimethyl adipate hydrogenation at presence of Pt based catalysts

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Abstract

Dimethyl adipate hydrogenations catalyzed by Pt/Al₂O₃ and Pt/TiO₂ have been studied. Catalysts were prepared with the conventional impregnation method. Physical–chemical characterization of the catalytic systems was made with the use of different techniques: N₂ and H₂ sorption, scanning electron microscopy (SEM), energy-dispersive electron (EDS) probe X-ray analysis, temperature programmed reduction (TPR) and inductively coupled plasma optics emission spectrometry (ICP-OES). Metals dispersion in the catalysts is directly related to the superficial area of the supports, and partially covered particles (in the case of the TiO₂) can be present. Support modifies the behavior of metals in its surface for different ways: SMSI effect (TiO₂) or acidity (Al₂O₃). The catalyst supported on Al₂O₃ is more active, reaching 52.91% conversion after 10 h of reaction, while at the same period of time, the catalyst supported on TiO₂ converted only 15.56% of the substrate. Methyl caproate, adipic acid mono-methyl ester and caprolactone were obtained as main products by Pt/Al₂O₃ catalyst. These products indicate that carboxylic groups have not been activated enough, leading to formation of significant amount of hydrogenation products different from 1,6-hexanediol (diol). Pt/TiO₂ catalyst obtained methyl caproate, caprolactone, hexane and diol, where hexane formation occurred from methyl caproate. Diol formation occurred after 5 h of reaction and it indicates participation of platinum and TiO₂ as active catalytic sites.

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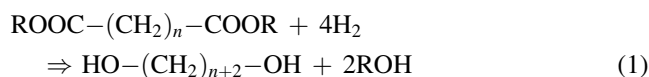
Keywords: Selective hydrogenation; Diol; Pt/TiO₂; Pt/Al₂O₃; Ester hydrogenation

1. Introduction

Diols are widely applied as raw material for the synthesis of polyesters, polyurethanes, varnishes, adhesives, textile auxiliaries, fragrances, pharmaceuticals, and recently, for the production of biodegradable polymers [1]. These materials can be obtained from the catalytic hydrogenation of dicarboxylic acids and esters. Catalysts commonly used consist of copper or zinc chromate [2], ruthenium dioxide [3] and rhenium heptoxide [4] under strict reactional conditions.

The 1,6-hexanediol obtained from catalytic hydrogenation of adipic ester is industrialized under reaction conditions where temperature and pressure rates vary from

443 to 513 K and from 150 to 330 atm, respectively. Moreover, the selective production of 1,6-hexanediol is a complex reaction, since various products can be obtained from its respective ester hydrogenation. Under hydrogenation conditions, esters originated from dicarboxylic acids can be transformed into their respective diols, or glycols, according to the equation:



Esters hydrogenation reaction is also called hydrogenolysis because before the atomic hydrogen addition there must be rupture of one of the links C–O or O–R on the ester. Thus, the reaction selectivity 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

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hydrocarbons. Therefore, the development of a selective catalytic system suits interest to the production of diol under less severe reactional conditions.

Catalytic hydrogenation reactions of polyfunctional compounds have been object of extensive series of researches, such as: oleic acid hydrogenation on impregnated catalyst Ru–Sn/TiO₂ [5] and on sol–gel Ru–Sn/Al₂O₃ [6], cinnamic aldehyde hydrogenation on Pt–Fe/TiO₂ [7], citral hydrogenation at presence of Rh–Sn/TiO₂ [8], Rh–Sn/SiO₂ [9] and Ru–Sn/TiO₂ [10] and dimethyl adipate hydrogenation by Ru–Sn [11].

Generally, the hydrogenation of molecules containing the carbonyl group is held at presence of catalysts supported by group VIII B metals, Ru, Rh, Pd, Os, Ir, Pt, Ni and Co. However, monometallic catalysts are not very effective regarding the selective attack of the carbonyl function [11]. Among those metals, Ru has shown better catalytic performance in reducing the occurrence of undesirable reactions, although none of the systems has led to 1,6-hexanediol formation. These systems selectivity can be modified by inserting a second metal considered inactive in hydrogenation reactions, such as Sn [12]. Ru–Sn/TiO₂ systems have shown to be active, though little selective to the formation of the desirable product, while Ru–Sn/Al₂O₃ systems have presented 22% selectivity diol [11]. In contrast, the use of TiO₂ as support on the cinnamic aldehyde hydrogenation has considerably increased the reaction selectivity to the corresponding alcohol [7].

This paper exploits platinum as active metal, and TiO₂ and Al₂O₃ 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 these catalysts on the selective hydrogenation of polyfunctional compounds. For instance, Pt–Fe/TiO₂ catalyst used by Silva et al. [10] on the cinnamic aldehyde hydrogenation, the Ru–Sn/TiO₂ catalyst used by Santos and co-workers [5] on the oleic acid, or even catalytic system Rh–Sn/TiO₂ applied by Lobão et al. [8] on the citral hydrogenation.

2. Materials and methods

2.1. Catalysts preparation

Catalysts were prepared with the impregnation method in aqueous suspensions, in order to obtain a catalyst with nominal concentration of 2% in platinum weight. Supports applied here were TiO₂ (Aldrich, >99%, crushed and strained in average fraction of 0.045 mm) and γ -Al₂O₃ (Degussa type 213, crushed and strained in average fraction of 0.045 mm), and the precursor salt used here was Pt(NH₃)₄Cl₂·0.68H₂O (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 dried in oven for 12 h,

at temperature of 393 K. Catalysts were then subjected to calcination by treatments for 4 h at 673 K, under flow of 50 mL min⁻¹ of synthetic air, and reduction for 2 h at 673 K, under flow of 40 mL min⁻¹ of 2% H₂ and 98% N₂ mixture.

2.2. Characterization

A Micrometrics ASAP 2010 device was used to obtain adsorption measures at temperature of 77 K, under pressure rate from 10 to 925 mmHg. Catalysts specific area was obtained by using the Brunauer, Emmett and Teller (BET) method.

Assays of temperature-programmed reduction (TPR) were held on quartz reactor, using 100 mg of catalysts 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 were recorded by using a Balzers Omnistar Quadrupole Mass Spectrometer, model QMS200, in function of temperature.

Scanning electron microscopy (SEM) was done with a Leica-Zeiss LEO 440 microscope, to which a Si(Li) energy dispersive analyst with Be window is attached, model Oxford 7060. Energy-dispersive electron (EDS) probe X-ray analysis was done with element mapping.

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 had been reduced “in situ” at 673 K for 2 h under flow of H₂ and the system was evacuated under flow of H₂ for 1 h until reaching the sorption temperature (308 K). The sorption measurements were obtained in pressures varying from 10 to 400 mmHg.

2.3. Catalytic tests

Dimethyl adipate hydrogenation was held on a high pressure Parr reactor, made of 316 stainless steel and equipped with mechanical stirring axe with speed setting. Reactions were carried out in liquid phase with 1,4-dioxane as suitable solvent to keep the reaction phase homogeneity. The system was kept at 523 K and 50 atm of H₂ [1], under constant mechanical agitation at speed of 1500 rpm. Agitation speed has been considered by Silva et al. [7] as enough to keep system free from diffusional limitations. Typically, 1.40 g of catalyst, 80 mL of 1,4-dioxane, 7.09 g of dimethyl adipate and 3.6 g of tetradecane (internal standard) were used. Samples were collected for each reaction for 15 h.

Reaction products quantification was done by using gas chromatography with a Thermo Quest Trace GC 2000 chromatograph having a capillary column HP1 and for internal standard, tetradecane. Identification of the products was previously held in a gas chromatograph attached to a mass spectrometer HP5988 A.

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