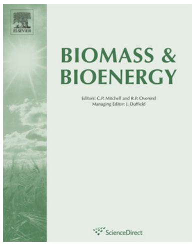
BIOMASS AND BIOENERGY 56 (2013) 592–599

Available online at www.sciencedirect.com

SciVerse ScienceDirect

http://www.elsevier.com/locate/biombioe



Improvement of the stability of basic mixed oxides used as catalysts for aldol condensation of bio-derived compounds by palladium addition

Laura Faba, Eva Díaz, Salvador Ordóñez[*]

Department of Chemical Engineering and Environmental Technology, University of Oviedo, (Faculty of Chemistry), Julián Clavería s/n, 33006 Oviedo, Spain

ARTICLE INFO

Article history:
Received 26 February 2013
Received in revised form
15 June 2013
Accepted 18 June 2013
Available online 4 July 2013

Keywords:
Base-metal bifunctional catalysts
Biomass upgrading
2nd Generation biofuels
Deactivation in aldol condensation reactions
Furfural
Hydrogen-promoted aldol condensation

ABSTRACT

Aqueous-phase aldol condensation of biomass-derived ketones and aldehydes is a key step in the preparation of fuels and chemicals from renewable resources. Furfural–acetone aldol condensation yielding C_8 and C_{13} adducts was studied at 323 K and 1 MPa in a stirred batch reactor. We propose a new strategy for minimizing catalytic deactivation, consisting of modifying catalysts ($MgO-ZrO_2$ and $MgO-Al_2O_3$) by Pd addition (2%). This modification slightly changes the morphology and surface chemistry of the supports, leading to changes on the catalysts performance but not reaction mechanism modifications. If condensation is performed in hydrogen atmosphere, the partial hydrogenation of the condensation adducts increases its water solubility, minimizing catalyst deactivation. In that way, the selectivity for C13 adduct decreases only 25% between two successive reaction cycles using Pd/$MgO-ZrO_2$ catalyst, whereas this decrease is of 90% for the un-doped mixed oxides. These effects are less marked for the $MgO-Al_2O_3$ catalyst.

1. Introduction

The depletion of fossil fuels reserves and the increasing environmental concerns about green house gases emissions have increased the development of the renewable energies. Among the different alternative sources, biomass is an excellent candidate to produce organic fuels at relevant amounts [1]. The production of 1st-generation liquid biofuels (obtained mainly from food crops such as sugar, oil and cereals) is already a mature technology. However, several drawbacks hinder its industrial development, such as the competition for land and water used for food, the high production and processing costs, and the low efficiency in terms of fraction of biomass carbon atoms transformed into fuels [2]. These disadvantages have stimulated the development of 2nd-generation liquid biofuels. In this way, lignocellulosic feedstock raw materials include by-products (cereal straw, forestry wastes), residues (organic components of municipal solid wastes), and dedicated feedstocks (purpose-grown vegetables).

Huber et al. [3] proposed a process which transforms the carbohydrates into C8–C13 alkanes. Cellulosic materials are

---

[*] *Corresponding author*. Tel.: +34 985 103 437; fax: +34 985 103 434.
E-mail address: sordonez@uniovi.es (S. Ordóñez).

http://dx.doi.org/10.1016/j.biombioe.2013.06.008

transformed by hydrolysis into sugars (C5–C6) and oxidized/dehydrated derivatives of these sugars (furfural, hydroximethylfurfural, etc.). Main chemical routes for the upgrading of these materials involve a first step of o-glycosidic bond hydrolysis, in order to obtain single sugars and functional intermediates of the furfural family [4–6]. These reactions can be performed by acid hydrolysis [7] or by catalytic alternatives, such as hydrolytic hydrogenation [4]. Further aldol condensation of these molecules with acetone and deep hydrogenation lead to C8–C13 *n*-alkanes, valuable as diesel-quality fuel [8]. During this hydrogenation, carbonyl functional groups are transformed firstly into hydroxyl groups, and secondly into linear alkanes by a desoxygenation.

The reaction between furfural and acetone yielding C_8, which subsequently reacts with another furfural molecule yielding the C_{13} adduct, is widely selected as a model aldol condensation reaction [3,9]. This reaction was firstly carried out using homogeneous catalysts, NaOH or $Ca(OH)_2$. However, the application of the Green Chemistry principles has encouraged the use of heterogeneous catalysts, such as nanosized Co–Al spinels or nitrogen-substituted zeolites [10], Mg–Zr mixed oxides [11], WO_3–ZrO_2 [12] or Mg–Al and Ca–Zr mixed oxides [13]. However, the challenge is still to find selective and stable catalysts, since significant deactivation by the strong adsorption of the reaction products on the catalyst surface of Mg–Zr and Mg–Al mixed oxides was observed [13]. Since the final step of the process consists of deep hydrogenation of C8 and C13 adducts using an active phase, such as Pd or Pt, integration of both processes is also very attractive. The combination of both reactions consecutively was already studied [8,12,14], but no data on conversions and selectivities were obtained after aldolization reaction. Furthermore, there are discrepancies about the influence of the incorporation of Pd on the surface properties of the basic catalysts, being some authors that observe a decrease in the surface are caused by a partial blockage of some pores [12] whereas other researches indicate that the metal can cause a swelling in the original structure [15,16].

The scope of the present work is to analyze the behavior of different bi-functional catalysts, Pd/MgO–ZrO_2 and Pd/MgO–Al_2O_3, containing palladium and basic sites, in the aldol condensation of furfural and acetone. The effect of palladium addition on the catalysts deactivation has been also studied. For this purpose, two situations were considered: performing the reaction at the same operation conditions used for unpromoted catalysts, and using a hydrogen atmosphere for promoting partial hydrogenation of the reaction intermediates.

2. Methods

2.1. Materials and chemicals

The MgO–Al_2O_3 mixed oxide was prepared using $Mg(NO_3)_2 \cdot 6H_2O$ (Fluka, >99%) and $Al(NO_3)_3 \cdot 9H_2O$ (Panreac, 98%), K_2CO_3 (Panreac, 99%) and a NaOH (Prolabo, 98%) solution. Magnesia–zirconia (MgO–ZrO_2) catalyst was synthesized using magnesium nitrate hexahydrate (Fluka, >99.0%), ziconyl nitrate (Aldrich, hydrated) and the NaOH (Prolabo, 98%) solution. The impregnation of Pd was done using a tetraaminopalladium (II) nitrate solution from Aldrich with a metal loading of 10% by weight.

Concerning to the reactants, furfural and acetone were supplied by Panreac (purity: 98 and 99.5%, respectively). For calibration, standards of the main products were used: furfurildeneacetone C8 (Alfa Aesar, 98%) and the dimer 1,5-bis(2-furanyl)-1,4-pentadien-3-one, C13 (Acros, 98%).

2.2. Catalyst preparation and characterization

The mixed oxides used as supports for bifunctional catalysts, MgO–ZrO_2 and MgO–Al_2O_3, were synthesized using the techniques described in our previous works [13,14]: Mg–Al mixed oxide by co-precipitation at low super-saturation method (Mg/Al atom ratio of 3), whereas the sol–gel technique was chosen to the Mg–Zr synthesis (Mg/Zr atom ratio of 4).

Bifunctional catalysts (Pd/Mg–Zr and Pd/Mg–Al, 2% mass fraction of Pd in both cases) were prepared by incipient wetness impregnation of the metal solution onto the supports. Resulting materials were treated in flowing He ($100\ cm^3\ min^{-1}$) with a 2 h ramp and held for 2 h at 723 K. Further reduction was carried out in flowing H_2 ($50\ cm^3\ min^{-1}$) with a heating rate of $5\ K\ min^{-1}$ from 293 K to 473 K, holding this temperature during 2 h.

Surface area and pore volume were measured by nitrogen adsorption at 77 K in a Micromeritics ASAP 2020 surface area and porosity analyzer. The crystallographic structures of the bifunctional catalysts were determined by XRD using a Philips PW 1710 diffractometer, working with the Cu-Kα line ($\lambda = 0.154$ nm) in the 2θ range of 5–85° at a scanning rate of $2°\ min^{-1}$. Likewise, the Pd particle morphology and size distributions were determined by transmission electron microscopy (TEM) in a MET JEOL-2000 EX-II microscope and by H_2 chemisorption at 373 K in the Micromeritics ASAP 2020 apparatus.

The strength and distribution of the basic/acid sites were determined by temperature programmed desorption of pre-adsorbed CO_2/NH_3 in a Micromeritics TPD/TPR 2900. Samples (10 mg) were pretreated in He at 723 K for 2.5 h and exposed to a CO_2 or NH_3 (2.5% NH_3 by volume in He) stream at 323 K until saturation coverage were reached. Weakly adsorbed CO_2 or NH_3 was removed by flushing with He at the same temperature for about 1.30 h. The temperature was then increased at a linear rate of $5\ K\ min^{-1}$ from 293 K to 723 K and the signal of CO_2 or NH_3 desorbed was monitored by mass spectrometry. The nature of basic sites was corroborated by CO_2 chemisorption analyzed by Fourier transform infrared (FTIR) spectroscopy, using a Bruker Vector 22 FTIR spectrophotometer (deuterated triglycine sulfate detector) in the 4000–400 cm^{-1} range, with a resolution of 2 cm^{-1} and using 100 scans.

The surface composition of the mixed oxides was measured by X-ray Photoelectron Spectroscopy (XPS), using an SPECS system equipped with a Hemispherical Phoibos detector operating in a constant pass energy, using Mg-Kα radiation ($h \cdot \upsilon = 1253.6$ eV).