



Catalysts based on Rh(III)-hexamolybdate/ γ -Al₂O₃ and their application in the selective hydrogenation of cinnamaldehyde to hydrocinnamaldehyde

Guillermo R. Bertolini^a, Carmen I. Cabello^{a,b,*}, Mercedes Muñoz^a, Mónica Casella^a, Delia Gazzoli^c, Ida Pettiti^c, Giovanni Ferraris^c

^a "Centro de Investigación y Desarrollo en Ciencias Aplicadas Dr. J. Ronco" (CINDECA-CCT CONICET La Plata – Universidad Nacional de La Plata), Calle 47 No. 257, 1900 La Plata, Argentina

^b Facultad de Ingeniería UNLP and Member CICPBA, Argentina

^c "Dipartimento di Chimica" La Sapienza Università di Roma, Piazzale Aldo Moro 5, I-00185 Roma, Italy

ARTICLE INFO

Article history:

Received 14 December 2011

Received in revised form

13 September 2012

Accepted 14 September 2012

Available online 25 September 2012

Keywords:

Heteropolyoxomolybdates

Anderson phases of Rh(III)

RhMo₆/ γ -Al₂O₃

Cinnamaldehyde

Selective hydrogenation

Hydrocinnamaldehyde

ABSTRACT

Several catalysts based on [RhMo₆O₂₄H₆]³⁻ (RhMo₆) heteropolyanion supported on γ -Al₂O₃ with different textural properties were prepared, characterized and tested in the liquid-phase hydrogenation of cinnamaldehyde. The characterization of pure and supported systems was carried out using several techniques including XRD, SEM-EDS microscopy, Raman microprobe, X-ray photoelectron spectroscopies and temperature programmed reduction (TPR). The catalytic performance was monitored by conversion of the starting cinnamaldehyde as a function of time: the initial activities represented as the turnover frequency (TOF), were measured considering the surface Rh atoms. The planar heteropolyanion RhMo₆/(E) based systems showed enhanced catalytic activity over the RhMo conventional catalyst obtained by successive impregnation of both transition metal ions (Rh(III) chloride and heptamolybdate). The selectivity for the RhMo₆ systems was mainly toward HCAL unlike the conventional catalyst which showed selectivity toward CA. This study also showed a synergistic effect between Rh and Mo through which Rh promoted Mo reducibility.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

The selective hydrogenation of α,β -unsaturated aldehydes assisted by supported metal catalysts is a key stage in the preparation of pharmaceutical products, flavors and fragrances [1–3]. The selective hydrogenation of cinnamaldehyde (CAL) is a good example of this commercially important reaction that allows the attainment of cinnamic alcohol (CA), hydrocinnamaldehyde (HCAL) and 3-phenyl propanol (PP). The cinnamic alcohol is a valuable product in the perfume industry for its aroma as well as for its fixation properties. Also, it is used in the pharmaceutical industry in the synthesis of chloromycetin antibiotic [4,5]. More recently, important applications were found for the hydrocinnamaldehyde used as intermediate in the synthesis of medicines for the treatment of HIV [6–8].

The hydrogenation process is a complex one when the molecule to be hydrogenated has two or more functional groups of comparable reactivity. This situation is present in molecules that have C=C and C=O conjugated groups such as α,β -unsaturated aldehydes or

ketones. An example is the selective hydrogenation of cinnamaldehyde (CAL) [9–12]. This species is a vinylic derived of benzaldehyde and the aldehyde group behaves with catalyst as if it were an aromatic aldehyde. The carbonyl group is reduced easily and competes with saturation of the C=C double bond [13]. The hydrogenation of CAL catalyzed by supported noble metals leads usually to a mixture of HCAL, CA and PP. The selectivity to CA is highly dependent on the nature of the precious metal used as catalyst [14], and the noble metals selectivity can be classified in the following sequence: Pd < Rh < Ru < Pt < Ir. Pd and Rh generally display high activity but rather poor selectivity toward cinnamyl alcohol and during the past few years, several examples of synthesis and properties of mono or bi metallic Pd catalysts for selective hydrogenation of CAL to HCAL have been reported [15–17]. Little has been published concerning the use of rhodium for the selective hydrogenation of CAL to HCAL. Additionally, it was found that the catalysts deactivation rate in monometallic systems is significant and hence a low stability derives [18]. Therefore, in the hydrogenation field, bimetallic catalysts are often used in order to improve selectivity and stability of a single component catalyst [19,20]. In general, supported bimetallic catalysts are very interesting materials because one metal can tune and/or modify the catalytic properties of the other metal as a result of both electronic and structural effects [20,21]. In this

* Corresponding author: Tel.: +54 221 4210711; fax: +54 221 4210711.
E-mail address: ccabello@quimica.unlp.edu.ar (C.I. Cabello).

sense, bi- or trimetallic catalytic systems based on heteropolyacids or polymetalates (HPOMs), both as bulk and supported systems, have started to replace a large number of conventional oxide precursors, improving the efficiency and environmental conditions of several catalytic processes [22].

Our recent studies have shown that Co, Ni or Rh containing heteropolymolybdates with Anderson-type structure are interesting precursors in heterogeneous catalysts for hydrotreatment processes [23,24]. Such studies have shown that the planar structure of the heteropolyoxoanion as well as its redox and solubility properties are relevant factors in the heteropolyanion-support interaction, producing an active surface with an ordered distribution and uniform deposition of the metallic elements, which favors the synergic effect.

In continuation of our studies of these phases as bimetallic catalytic precursors, in the present paper we have studied the selective hydrogenation of CAL by using catalysts based on Anderson-type heteropolyoxometalates with formula $(\text{NH}_4)_3[\text{RhMo}_6\text{O}_{24}\text{H}_6] \cdot 7\text{H}_2\text{O}$ supported on $\gamma\text{-Al}_2\text{O}_3$. The $\text{RhMo}_6/\gamma\text{-Al}_2\text{O}_3$ systems resulted active and selective for the hydrogenation of CAL to HCAL and their performance were compared with those of a conventional $\text{RhMo}/\gamma\text{-Al}_2\text{O}_3$ catalyst, prepared by successive impregnation.

2. Experimental

2.1. Catalyst preparation

The synthesis of the precursor with formula $(\text{NH}_4)_3[\text{RhMo}_6\text{O}_{24}\text{H}_6] \cdot 7\text{H}_2\text{O}$ (RhMo_6) was carried out from the aqueous solution reaction of ammonium heptamolybdate and $\text{RhCl}_3 \cdot 6\text{H}_2\text{O}$ in stoichiometric proportions, as previously reported [23,24].

In order to analyze the support effect, we selected an alumina support thermally treated at 773 K in air for 24 h (hereafter B) and two types of commercial $\gamma\text{-Al}_2\text{O}_3$ spherulite, hereafter EI and EII from YPF Oil Company (Yacimientos Petrolíferos Fiscales Argentina). The procedure adopted for the catalyst preparation was the equilibrium adsorption impregnation using heteropolymolybdate aqueous solution prepared as previously reported [24,25]. The RhMo_6 catalysts were obtained by adding 10 mg Mo/mL of RhMo_6 aqueous solution to $\gamma\text{-Al}_2\text{O}_3$ (EI and EII types) and Al_2O_3 (B) supports to obtain catalysts with ca. Mo 6 wt% and Rh 1 wt%, and drying at 353 K. The resulting samples were labeled $\text{RhMo}_6/\text{E(I)}$, $\text{RhMo}_6/\text{E(II)}$ and $\text{RhMo}_6/\text{(B)}$, respectively.

A conventional RhMo catalyst was prepared by successive impregnation of type (B) alumina, in excess of pore volume. According to a literature method [21] this catalyst was obtained by first adding the $\text{RhCl}_3 \cdot 6\text{H}_2\text{O}$ solution to the support and drying at 353 K. The solid was then impregnated with a $(\text{NH}_4)_6[\text{Mo}_7\text{O}_{24}] \cdot 4\text{H}_2\text{O}$ (AHM) solution and dried at 353 K. The resulting sample, containing 6% of Mo and 1% of Rh, was labeled $\text{RhMo}/\text{(B)}$.

Before the catalytic tests, all catalysts were pretreated in a flow of H_2 , at 623 K, for 2 h.

2.2. Chemical analysis

The Mo and Rh content was determined by atomic absorption spectrometry (AAS), using an IL-457 spectrometer, on initial (C_i) and final (C_f) solutions. The Mo and Rh adsorbed concentrations (C_a^{Mo} or C_a^{Rh}) were calculated from experimental C_i (initial) and C_f (final) data, taking into account the volume of the impregnated solution and the support mass (mass balance) according to the expression:

$$C_a = \left\{ \frac{(C_i - C_f \times V)}{m} \right\} \times 100.$$

2.3. Characterization of catalysts

X-ray powder diffraction patterns were recorded in the 2θ angular range from 5° to 70° by a diffractometer Philips PW 1714 using Cu $K\alpha$ radiation (Ni filter).

Scanning electron microscopy (SEM) with EDS analysis was performed by a Microscope Philips SEM 505 with dispersive energy system for microanalysis, EDAX 9100.

Raman spectra were collected on powder samples at room temperature in the back-scattering geometry with an in Via Renishaw spectrometer equipped with an air-cooled CCD detector and a super-Notch filter. The emission line at 514.5 nm from an Ar^+ ion laser was focused on the sample under a Leica DLML microscope using a $20\times$ objective. Five 20-s accumulations were attained for each sample with an incident beam power of about 5 mW. The spectral resolution was 2 cm^{-1} and the spectra were calibrated using the 520.5 cm^{-1} line of a silicon wafer.

XPS spectra were measured on a Leybold–Heraeus LHS10 spectrometer in FAT mode (50 eV pass energy) with Mg $K\alpha$ radiation (12 kV, 20 mA) at a pressure lower than 10^{-9} Torr. The samples, manually pressed onto a gold plate, were analyzed as prepared and after treatment in H_2 outside the spectrometer. The Rh3d, Mo3d, O1s, C1s and Al2p regions were processed by computer. Electron binding energies were referenced to the C1s peak at 285.0 eV. The intensity ratios, $I_{\text{Me}}/I_{\text{Al}}$, (Me = Rh or Mo) were obtained from peak area determination by integration of the appropriate peak after smoothing and nonlinear Shirley-type background subtraction by Esca Tools 4.2 software (Surface Interface, Inc., Mountain View, CA). To assess a quantitative relationship between the XPS peak intensity ratio and surface composition, the experimental results were compared with the values predicted by the sensitivity factor, S , approach firstly proposed by Wagner et al. [26].

Surface area measurements, Brunauer–Emmett–Teller (BET) [27] multipoint method, and textural analysis were obtained using a Micromeritics ASAP 2020 equipment. The samples were pretreated under vacuum in two stages of 1 h at 373 and 573 K. The pore distribution was determined by the Barret–Joyner–Halenda (BJH) method [28] from the analysis of micropore isotherm by the t -test [29] taking the curve of Harkins and Jura [30]; the total pore volume was determined by the rule of Gurvitsch [31].

The temperature programmed reduction (TPR) diagrams were obtained in a flow system with a mixture of 10% volume H_2 and 90% N_2 volume (20 cm^3/min), by heating from room temperature up 1123 K at 10 K/min with a Quantasorb Jr. (Quantachrome) equipment.

Measurements of Rh dispersion were made following the Boudart method: Rh dispersion, defined as the ratio of the exposed Rh atoms to the number of total Rh atoms, was determined by H_2/O_2 titration [32] using a volumetric apparatus. The fresh samples (typically 0.5–1 g, depending on Rh content) were pretreated in flowing N_2 at 423 K for 30 min, reduced in H_2 (10% in He) at 623 K for 1 h and then purged with N_2 at 623 K for 1 h before cooling down to RT in N_2 . Samples were then exposed to O_2 (10% in N_2) at RT for 30 min, and flushed with N_2 for 30 min at RT. After careful evacuation at RT down to 1 Pa, the irreversibly adsorbed H_2 at RT, H_{irr} , was determined. In particular, total H_2 uptakes were determined by zero pressure extrapolation of the adsorption isotherm, usually in the hydrogen pressure range 6.6–26.6 kPa. Samples were subsequently evacuated at RT for 0.5 h and a second isotherm due to the reversible part of the adsorption was determined. The difference between the total (first isotherm) and the reversible (second isotherm) uptakes in the parallel and linear part of the isotherms gave the irreversible part of the adsorption (double isotherm method). The exposed Rh atoms, Rh_s , were then calculated from H_{irr} (irr=irreversible), assuming a $H_{\text{irr}}/\text{Rh}_s$ ratio of 1 and by taking into account the

Download English Version:

<https://daneshyari.com/en/article/65945>

Download Persian Version:

<https://daneshyari.com/article/65945>

[Daneshyari.com](https://daneshyari.com)