Applied Catalysis B: Environmental 154–155 (2014) 190–196

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Mesoporous tantalum oxide as catalyst for dehydration of glucose to 5-hydroxymethylfurfural

I. Jiménez-Morales, M. Moreno-Recio, J. Santamaría-González,
P. Maireles-Torres, A. Jiménez-López*

Universidad de Málaga, Departamento de Química Inorgánica, Cristalografía y Mineralogía (Unidad Asociada al ICP-CSIC), Facultad de Ciencias, Campus de Teatinos, 29071 Málaga, Spain

ARTICLE INFO

Article history:
Received 3 December 2013
Received in revised form 5 February 2014
Accepted 12 February 2014
Available online 20 February 2014

Keywords:
Mesoporous tantalum oxide
5-Hydroxymethylfurfural
Glucose dehydration
Levulinic acid

ABSTRACT

Mesoporous tantalum oxide was prepared by acid hydrolysis of tantalum penta-ethoxide in the presence of a triblock co-polymer Pluronic L-121, a non-ionic surfactant, at room temperature and subsequent calcination at 550 °C for 6 h. This solid exhibits a suitable specific surface area (79 $m^2\,g^{-1}$) and a high acidity (353 μmol $NH_3\,g^{-1}$) with the presence of both Brönsted and Lewis acid sites, demonstrating to be active as solid acid catalyst in the dehydration of glucose to 5-hydroxymethylfurfural (HMF), in a biphasic water/methyl-iso-butyl ketone (MIBK) system. Thus, by using a glucose:catalyst weight ratio of 3:1, a glucose conversion of 69% and a HMF yield of 23% were achieved at 175 °C, and after only 90 min of reaction time. The catalytic process is selective toward HMF, which is preserved from ulterior hydration to levulinic acid. Fructose was also detected as by-product of glucose isomerisation with 14% of selectivity. The catalyst is very stable, since no leaching of tantalum species to the liquid phase was found; moreover, the catalytic performance of this acid solid is well recovered after calcination at 550 °C for 2 h.

1. Introduction

The increasing oil prices and the diminishing fossil fuel reserves, as well as the growing concern about global warming, have led to the search of new sustainable sources of energy from renewable materials. Biomass can be considered as a renewable feedstock that can be used for fuel and chemical production, taking advantage from its abundance and relative low cost. For instance, platform chemicals and biofuel production from waste lignocellulosic biomass is an attractive alternative to fossil-based feedstocks. The main products obtained from agriculture waste and energy crops consist of cellulose (40–50%), hemicellulose (25–35%) and lignin (5–20%), being glucose the building block of cellulose [1]. High glucose yields are achieved via enzymatic hydrolysis of cellulose, although it can be also carried out under harsher conditions using solutions of mineral acids at elevated temperatures.

Among current biofuel sources, one of the most important building blocks is 5-hydroxymethylfurfural (HMF) obtained from biomass, which is a versatile and key intermediate for the production of a wide variety of biobased chemicals [2] (e.g. levulinic acid, furandicarboxylic acid, dimethyl furan, γ-valerolactone and dihydroxymethylfurfural) and it is attracting much attention in biofuels and chemical industry [3,4]. HMF can be easily prepared by triple dehydration of fructose catalysed by mineral acids; however, starting from saccharides, special catalysts are required to perform the glucose dehydration to HMF.

Besides mineral acids, other catalysts have been employed to obtain HMF, such as metal salts in non-aqueous solvents (DMSO) [5], Lewis acids from different metallic salts in acid medium [6], lanthanide salts in biphasic solvent systems [7] or in ionic liquids [8]. However, all these catalytic systems have important drawbacks associated to the high cost of ionic liquids and high energy consumption in the case of organic solvents. For industrial applications, heterogeneous catalysts are recommended due to their low cost and their easy recovery from reaction medium. Recently, several compounds based on elements of the 5th group of the Periodic Table have been employed as catalysts for the preparation of HMF. Thus, the so-called "niobic acid" ($Nb_2O_5 \cdot nH_2O$) is an amorphous solid with strong acidic properties due to the presence of highly polarized water molecules, which has been used for dehydration of mono- and polysaccharides to HMF at 160 °C in a biphasic water-2-butanol system, attaining a HMF yield of 46% from glucose [9]. This solid was also studied by Carniti et al. [10] in this reaction,

---

* Corresponding author. Tel.: +34 952131876; fax: +34 952131870.
E-mail address: ajimenezl@uma.es (A. Jiménez-López).

http://dx.doi.org/10.1016/j.apcatb.2014.02.024

observing the absence of side-reaction in the dehydration of fructose to HMF in water at 100 °C. This catalytic activity of $Nb_2O_5 \cdot nH_2O$ has been mainly attributed to the presence of water tolerant Lewis acid sites [11].

Moreover, a surface treatment of niobic acid with phosphoric acid led to an enhancement of the surface acidity, and therefore of its catalytic activity [12,13]. Different works have dealt with this niobic acid promoted with phosphoric acid catalyst, under batch conditions at 110 °C [14,15], or in a continuous reactor line at 90–110 °C [16]; all of them have reported high catalytic activity in the selective fructose dehydration to HMF. This high activity is justified by a synergy effect between a protonated phosphate group and a nearby metal Lewis acid site [17].

In a similar way, hydrated tantalum oxide ($Ta_2O_5 \cdot nH_2O$) displays strong acidity in its amorphous form and good activity in the dehydration of fructose at 160 °C [18]. The catalytic performance is clearly improved when this solid is treated with phosphoric acid at 300 °C, achieving a HMF yield of 58% when the substrate was glucose.

The aim of the present work is the preparation of a mesoporous tantalum oxide and its application to the dehydration of glucose to HMF in a biphasic water/methyl-iso-butyl ketone system. The use of ordered mesoporous catalysts presents significant advantages with respect to conventional ones, due to their high specific surface area and large pore size, which lead to a better diffusion of reactants and products [19]. In this study, the influence on the catalytic behavior of different experimental parameters, such as reaction temperature and time, percentage of catalyst and reutilization, has been evaluated in order to attain high HMF productivity values.

2. Experimental

2.1. Synthesis of mesoporous tantalum oxide

Mesoporous tantalum oxide was synthesized via a surfactant-assisted sol–gel process, in a similar way to the reported synthesis of other mesoporous oxides of niobium and tantalum [20,21], but following the modification introduced by Xu et al. [22]. Thus, a tri-block co-polymer Pluronic L-121 (Sigma-Aldrich) and $Ta(OC_2H_5)_5$ were employed as structure-directing agent and inorganic precursor, respectively. In a typical synthesis, 1 mmol of tantalum penta-ethoxide and 2 mL of 2 M hydrochloric acid aqueous solution were added to an ethanol solution containing 0.25 g of surfactant, under inert atmosphere. After stirring for 30 min, the resulting gel was aged at 40 °C for 24 h. Finally, the gel was dehydrated under vacuum at 60 °C to obtain a white solid. The surfactant was eliminated by calcination at 550 °C for 6 h. The obtained mesoporous tantalum oxide was kept in equilibrium with an atmosphere of 55% humidity.

To improve the acidity of this mesoporous tantalum oxide, 1 g of this solid was treated with a 1 M H_3PO_4 aqueous solution for 24 h, at room temperature. After drying at 60 °C, the solid was calcined at 300 °C for 2 h. Another catalyst was prepared in a similar way, but drying the sample at 85 °C for 2 h, without the calcination step.

2.2. Characterization techniques

Powder X-ray diffraction (XRD) patterns of catalysts were obtained on a PAN analytical X'Pert Pro automated diffractometer. They were recorded in Bragg-Brentano reflection configuration by using a Ge (1 1 1) primary monochromator (Cu $K\alpha_1$) and the X'Celerator detector with a step size of 0.017° (2θ), between 10° and 70° in 2θ with an equivalent counting time of 712 s step^{-1}. To investigate the formation of possible crystalline phases from mesoporous tantalum phosphate a thermodiffractometric study was carried out using an Anton Paar HTK1200 Camera under static air. A gas flow was not employed to avoid sample dehydration prior to the diffraction experiment. Data were collected at temperature intervals of 100 °C, ranging between 100 and 900 °C with a heating rate of 10 °C min^{-1}, and maintaining 15 min at each temperature to ensure thermal stabilization. The data acquisition range was 8–70° (2θ), with a step size of 0.017°.

Thermogravimetric (TG) and differential thermal analysis (DTA) of catalyst precursors were performed from room temperature until 850 °C on a SDT Q600 apparatus from TA Instruments, by using calcined alumina as reference and a heating rate of 10 °C min^{-1}. Textural properties of catalysts were obtained by nitrogen adsorption at liquid nitrogen temperature with a Micromeritics ASAP 2010 apparatus, after degassing the samples at 350 °C overnight. The accumulated pore volumes were determined by BJH method. Temperature programmed desorption of ammonia (NH_3-TPD) was used to determine the total acidity of the samples. Before the adsorption of ammonia at 100 °C, samples were heated from room temperature to 550 °C, with a heating rate of 10 °C min^{-1} and maintaining the sample at 550 °C for 1 h. The NH_3-TPD was performed between 100 and 550 °C with a heating rate of 10 °C min^{-1}, and the amount of desorbed ammonia was analyzed by an on-line chromatograph provided with a TC detector. FTIR spectra of adsorbed pyridine were recorded on a Shimadzu Fourier Transform Infrared Instrument (FTIR-8300). Self supported wafers of the samples with a weight/surface radio of about 15 mg cm^{-2} were placed in a vacuum cell greaseless stopcocks and CaF_2 windows. The samples were evacuated at 150 °C and 10^{-2} Pa overnight, exposed to pyridine vapors at room temperature for 15 min and then outgassed at different temperatures. Raman spectra were obtained with a Raman Senterra (Bruker) micro-spectrometer equipped with a thermo-electrically cooled CCD detector. Excitation radiation at 1064 nm was used as supplied from a Praseodimium laser. Raman spectra were performed from powder samples without any previous treatment.

X-ray photoelectron spectra were obtained using a Physical Electronics PHI 5700 spectrometer with non-monochromatic Al K_α radiation (300 W, 15 kV, 1486.6 eV) with a multi-channel detector. High resolution spectra were recorded at 45° take off-angle by a concentric hemispherical analyzer operating in the constant pass energy mode at 29.35 eV, using a 720 μm diameter analysis area. Charge referencing was done against adventitious hydrocarbon (C 1s at 284.8 eV). A PHI ACCESS ESCA-V6.0F software package was used for acquisition and data analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gaussian–Lorentzian curves in order to determine more accurately the binding energy of the different element core levels.

2.3. Catalytic test

For the dehydration reaction of glucose, a two-phase reactor system, consisting in water-MIBK, was used. MIBK was introduced to promote the dehydration reaction by shifting the equilibrium toward the formation of HMF, by extracting it immediately under stirring. In this way, HMF degradation can be avoided [23,24]. The catalytic reaction was carried out in a glass reactor of 15 mL, provided with a screw top of Teflon, at 175 °C and 90 min of reaction time, with a stirring rate of 600 rpm. Zero time was taken when temperature of the reactor reached 175 °C. The reaction was performed by using 50 mg of catalyst, 0.15 g of substrate in deionized water (1.5 g) and 3.5 mL of MIBK. After reaction time, this was quenched by introducing the reactor in a bath with cooled water; the liquid phases were separated and filtered, and the analysis of products was done in both phases. Glucose conversion and the product selectivity were calculated according to the following