Catalysis Communications 30 (2013) 5–13

Contents lists available at SciVerse ScienceDirect

Catalysis Communications

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

Short Communication

Relation between surface acidity and reactivity in fructose conversion into 5-HMF using tungstated zirconia catalysts

R. Kourieh [a], V. Rakic [b], S. Bennici [a], A. Auroux [a,*]

[a] Université Lyon 1, CNRS, UMR 5256, IRCELYON, Institut de recherches sur la catalyse et l'environnement de Lyon, 2 avenue Albert Einstein, F-69626 Villeurbanne, France
[b] Faculty of Agriculture, University of Belgrade, Nemanjina 6, 11080 Zemun, Serbia

ARTICLE INFO

Article history:
Received 26 April 2012
Received in revised form 27 September 2012
Accepted 9 October 2012
Available online 15 October 2012

Keywords:
Tungsten oxide
Zirconia supported catalysts
Surface acidity/basicity
Adsorption microcalorimetry
Catalytic fructose dehydration

ABSTRACT

Catalytic dehydration of fructose and its conversion to 5-hydroxymethylfurfural was studied using tungstated zirconia oxides, with various tungsten oxide loadings (1–20 wt.%). The samples were prepared by incipient wetness impregnation and thoroughly characterized using a combination of different techniques: structural, thermal and calorimetric analyses. Zirconia was predominantly present in the investigated samples in the tetragonal phase when the WO_3 loading was above 10 wt.%. The samples exhibited amphoteric characteristics, as they adsorbed both ammonia and sulfur dioxide on their surface. The number of surface acid sites increased with increasing WO_3 content. Fructose dehydration tests evidenced the formation of 5-hydroxymethylfurfural and by-products (formic and levulinic acids). The results show that the ratio of basic to acidic sites of the solid catalysts is the key parameter for the selectivity in 5-HMF, while the global fructose conversion was mainly related to the presence of acid sites of a given strength with $150 > Q_{diff} > 100$ $kJ \cdot mol_{NH_3}^{-1}$.

1. Introduction

The demand for energy is increasing continuously at a high rate in our global society which is rapidly evolving. Since petroleum is a dwindling source of energy, and having in mind all environmental considerations (defined, for example, by Kyoto protocol), there is a strong worldwide desire to reduce dependence on crude oil. Therefore, the need to search for renewable alternative energy systems has been imposed. Some of the alternative sources (like: solar, wind, hydroelectric, nuclear…) are carbon-free; however, their application in the transportation sector appears not to be easily feasible. Consequently, there is a need for carbon-based sustainable alternatives to petroleum-derived fuels. As a result, there is a growing interest to produce so-called biofuels from vegetable biomass, which is abundant, renewable and distributed widely in nature [1,2].

Vegetable biomass is generated from carbon dioxide and water, using sunlight as an energy source and producing oxygen as a subproduct. As primary products, this process gives monosaccharides (C_5 and C_6 sugars), while further transformations produce polymerized molecules (cellulose and hemicellulose) and cross-linked polymers (lignin). Evidently, biomass can be comprehended as a source of carbohydrates that can be transformed into families of useful or potentially useful substances. Hence, in recent years, there are numerous literature reports that present biomass as a sustainable source of carbon-based precursors and/or chemical intermediates, that can give a variety of valuable chemicals and fine chemicals [1–4]. Besides, main monosaccharides that can be found in biomass, glucose and fructose, can be used to produce liquid fuels — bioethanol and biodiesel. In fact, since direct production of biofuels from C_5- and C_6-sugars is difficult, recent efforts have been focused on converting them to one derivative of furan (5-hydroxymethylfurfural, 5-HMF), a compound which has been found to be a key intermediate between biomass-based carbohydrates and desired products such as chemicals and biofuels. It has been found that 5-HMF can serve as a precursor to numerous products and chemical intermediates related to fuel, polymer, and pharmaceutical industries [5–10]. As an illustration, Dumesic et al. raised the challenge to use 5-HMF as an intermediate to produce liquid-fuel, alkanes, and hydrogen from renewable biomass resources [11–16].

It is well known that 5-HMF can be obtained by acid catalyzed dehydration of fructose, glucose, sucrose and even cellulose; these processes are usually carried out in aqueous media with an added mineral acid. In fact, current attempts to produce 5-HMF have mainly focused on fructose as a starting material, in spite of its high cost. A drawback of acid catalysis in aqueous media is production of various side reactions, including further hydrolysis of 5-HMF to levulinic acid, that lowers its yield and increases the cost of product purification [17,18]. It is known that separation of 5-HMF from levulinic acid is particularly difficult [18]. In order to facilitate the purification of furan derivatives such as 5-HMF, the procedure of phase coupling can be applied [3,19]. Recent works proved that high yields of 5-HMF can be achieved in a biphasic reactor, where one phase contains aqueous solution of fructose and acid catalyst, while the other, the extracting phase, contains low boiling partially miscible organic solvent [19].

---

* Corresponding author. Tel.: +33 472 445398; fax: +33 472 445399.
E-mail address: aline.auroux@ircelyon.univ-lyon1.fr (A. Auroux).

1566-7367/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.catcom.2012.10.005

Recently, many research groups have published high-yield conversion of both glucose and fructose into HMF in ionic-liquid solvents, among them Zhao et al. [18] and Yong et al. [20–22]. However, these processes have disadvantages, such as a high cost due to several separation processes, expensive solvents, and materials corrosion. Conversion of fructose to 5-HMF was probed also in highly polar organic solvents, e.g. DMSO [17,23]. In addition, highly concentrated melt systems consisting of choline chloride, carbohydrate and different acidic catalysts have been reported as systems that express low environmental impact, giving satisfactory yields of 5-HMF [24].

Apart from these attempts to perform dehydration of sugars in homogeneous systems, there is still a possibility to provide a source of needed acidity using heterogeneous catalytic systems as an environmentally benign alternative, which offers also the possibility of easy catalyst separation, regeneration, and low cost procedure. Up to now, several solid catalysts known to express surface acidity have been tested in dehydration of monosaccharides. For example, sulphated alumina zirconia has shown 56% yield of HMF from fructose at 150 °C [25] and sulphated zirconia has shown 36% yield even at high reaction temperature [23], in comparison with about 20% yield of HMF found for TiO_2/ZrO_2 at 200 °C [26], and the yield of 50% found in the case of zirconium phosphate at 230 °C [27]. Promising yields (89% from fructose, 49% from glucose, 54% from inulin and 65% from hydrolyzed juice of Jerusalem artichoke) have been obtained using hydrated niobium pentoxide as a catalyst [28]. Recently, sulfonated organic heterpolyacid salt has also been reported as promising catalysts in fructose dehydration to 5-HMF [29]. From a brief insight into the reported results, it becomes evident that the activity and selectivity of most solid acid catalysts were found to give unsatisfactory results in water, even at high reaction temperatures [23].

In the present work, we performed the dehydration of fructose using solid WO_3-based catalysts, known to possess highly acidic surface sites. In order to tune the acidity, we have prepared a series of tungstated zirconia catalysts with various tungsten oxide loadings, using incipient wetness impregnation. Importantly, it is already known that the acid site strength of the tungsten/zirconia materials is similar or slightly higher than that found in zeolites or sulfated zirconia and is comparable to sulfuric acid [30]. WO_3/ZrO_2 catalysts are commonly used in a number of industrially important reactions, including hydration of carbohydrate, selective oxidation, paraffin isomerization, cracking, alkylation, liquid-phase Beckmann rearrangement of cyclohexanone oxime and for biodiesel synthesis through esterification and transesterification of fatty acids [31–36]. For many of these catalytic applications, the acidity of the supported tungsten oxide phase plays a crucial role in the overall catalytic activity [37]. A fundamental understanding of the WO_3 dispersed phase evolution on zirconia has been presented in the literature by many authors and recently reviewed by Iglesia [38], with particular attention to the influence of the sizes and structural compositions of the active catalytic domains on the catalytic activity. It has been found that the structure, electronic properties, and consequent catalytic function of small oxide domains depend sensitively on their surface densities (size and dimensionalities), on their composition, and on their specific connectivity to less active oxides typically used as supports [38].

Solids prepared in this work were fully characterized in terms of their structural and surface acid/base properties. The influence of surface and acid/base properties on the performance of these WO_3-based catalysts in fructose dehydration is discussed; in particular correlations have been established between the number and strength of acid/base sites and the 5-HMF selectivity and fructose conversion.

2. Experimental

2.1. Materials

WO_3 was purchased from Fluka (99.9% WO_3). $Zr(OH)_4$ was supplied by MEL-Chemicals (XZO 880/01), while ammonium metatungstate hydrate $(NH_4)_6H_2W_{12}O_{40}\cdot nH_2O$ was purchased from Fluka (≥99.0% WO_3-based on calcined substance, gravimetric), 5-HMF and fructose were purchased from SAFC (≥99% purity) and SIGMA (≥99% purity), respectively. Deuterium oxide (heavy water) was purchased from ALDRICH (99.9 atom % D).

2.2. Catalyst preparation

WO_3/ZrO_2 catalysts were prepared by wetness impregnation method. $Zr(OH)_4$ was impregnated with an ammonium metatungstate hydrate solution, to have a WO_3 loading ranging from 1 to 20 wt.%. The prepared solids are denoted by m-WO_3/ZrO_2, where m indicates the percentage of WO_3 wt.%. The resulting materials were air dried overnight at 85 °C, then calcined in flowing air for 4 h at 700 °C. This calcination temperature has been chosen on the basis of TG measurements, performed using Labsys-TG from Setaram. The crude samples (~50 mg) were heated from 25 to 900 °C with a heating rate of 5 °C min^{-1} in a flow of air, which was chosen as a soft oxidizing agent for calcination. The pure zirconia sample was also calcined at 700 °C.

2.3. Catalyst characterization

Elemental analysis was performed using ICP optical emission spectroscopy (ICP-OES) with an ACTIVA spectrometer from Horiba JOBIN YVON, after the samples were dissolved by appropriate solution of $NaOH + KNO_3$.

The surface areas, pore volumes and pore sizes were measured by nitrogen adsorption at −196 °C on a Micromeritics 2010 apparatus after heat pre-treatment under vacuum for 2 h at a temperature of 400 °C. Surface areas were determined by the BET method from the resulting isotherms. Pore volumes and pore sizes were determined by the BJH method.

The X-ray diffraction (XRD) measurements were carried out on a Bruker D5005 powder diffractometer scanning from 3° to 80° (2θ) at a rate of $0.02°\,s^{-1}$ using a Cu Kα radiation (λ = 0.15418 nm) source. The applied voltage and current were 50 kV and 35 mA, respectively.

The recording of transmission electron micrographs (TEM) was carried out using a JEOL 2010 LaB6 equipment operating at 200 kV with an energy dispersive X-ray spectrometer (EDS), (Link ISIS from Oxford Instruments). The samples were dispersed in ethanol using a sonicator and a drop of the suspension was dripped onto a carbon film supported on a copper grid and then ethanol was evaporated. EDS study was carried out using a probe size of 15 nm to analyze borders and centers of the particles and the small particles.

The X-ray photoelectron spectra (XPS) were obtained on a KRATOS AXIS Ultra DLD spectrometer equipped with a hemispherical electron analyzer and an Al anode (Al Kα = 1486.6 eV) powered at 150 W, a pass energy of 20 eV, and a hybrid lens mode. The detection area analyzed was 700 μm × 300 μm. Charge neutralization was required for all samples. The peaks were referenced to the C–(C, H) components of the C 1s band at 284.6 eV. Shirley background subtraction and peak fitting to theoretical Gaussian–Lorentzian functions were performed using an XPS processing program (Vision 2.2.6 KRATOS). The residual pressure in the spectrometer chamber was 5×10^{-9} mbar during data acquisition.

Raman spectroscopy measurements were performed using a LabRAM HR (Jobin Yvon) spectrometer. The excitation was provided by the 514.5 nm line of an Ar^+ ion laser (Spectra physics) employing a laser power of 100 μW. The laser beam was focused through microscope objective lenses (100×) down to a 1 μm spot on the sample. For each solid, the spectra were recorded at several points of the sample to ascertain the homogeneity of the sample; the average of these spectra was plotted and is discussed below.

Temperature-programmed reduction (TPR) was performed using a TPD/R/O-1100 instrument (ThermoFisher). Prior to the TPR run, the fresh sample was treated in a stream of O_2/He (0.998% v/v,