



Niobium oxides: Correlation of acidity with structure and catalytic performance in sucrose conversion to 5-hydroxymethylfurfural



Hannah Theresa Kreissl^a, Keizo Nakagawa^{a,b}, Yung-Kang Peng^a, Yusuke Koito^a, Junlin Zheng^c, Shik Chi Edman Tsang^{a,*}

^a Wolfson Catalysis Centre, Department of Chemistry, University of Oxford, Oxford OX1 3QR, UK

^b Department of Advanced Materials, Institute of Technology and Science, Tokushima University, Tokushima 770-8506, Japan

^c Shanghai Research Institute of Petrochemical Technology SINOPEC, Shanghai 201208, China

ARTICLE INFO

Article history:

Received 16 January 2016

Revised 3 March 2016

Accepted 4 March 2016

Available online 8 April 2016

Keywords:

Niobium oxide

Lewis/Brønsted acidity

Structure–acidity relation

Sugar conversion

Green chemistry

ABSTRACT

The conversion of sugars to 5-hydroxymethylfurfural (HMF) over solid acids in water represents an environmentally and separation-friendly route to an important platform molecule. In particular, the conversion of sucrose attracts increasing attention because it is cheaper and more widely available than glucose and fructose. Sucrose can undergo rapid hydrolysis to the two monosaccharides, however conversion mechanisms and interactions with solid acids remain unclear. Here, it is shown that niobium oxides possess Brønsted acid (BA) and Lewis acid (LA) sites of tunable quantity and strength, dependent on their structure and morphology. By systematically studying these acid catalysts, it is revealed for the first time that both acid type and strength are significant for the sugar conversion: Fructose reaction is catalyzed by BA, with weaker BA sites being more selective toward HMF. Glucose conversion to HMF involves an additional isomerization step to fructose, which can be catalyzed by both LA and strong BA but LA is more efficient. Sucrose is shown to be easily hydrolyzed into glucose and fructose under the reaction conditions and HMF is formed from the further conversion of the two sugars. It is demonstrated that mesoporous niobium oxide gives the highest HMF yield for sucrose conversion among all niobium oxides due to balanced BA and LA sites with appropriate acid strengths.

© 2016 Elsevier Inc. All rights reserved.

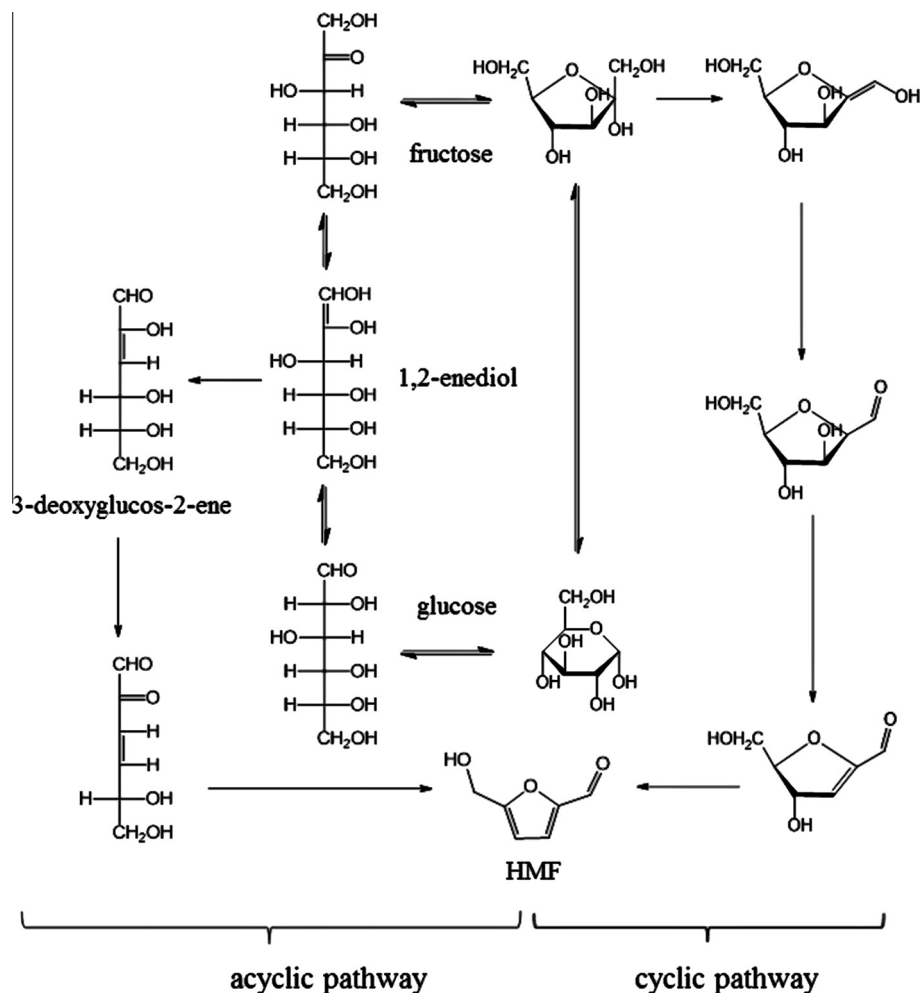
1. Introduction

Fossil fuels are currently the main source of both energy and platform molecules for the chemical industry. Rapidly decreasing reserves and growing economic demands raise the need for alternative sources. Biomass is a desirable choice as there is no net carbon emission upon its use. Extensive research over past years has led to the establishment of possible routes to convert biomass to fuels and process chemicals [1–4]. 5-hydroxymethylfurfural (HMF), derived from sugar molecules, is one of the most promising platform molecules. Various acid catalysts, both homogeneous and heterogeneous, have been employed to convert sugar molecules to HMF. Including the use of different solvents, reaction conditions and types of sugar, large amounts of data have been accumulated [5–10]. Disregarding the type of catalysts used, it has been found that HMF yield differs significantly with the type of sugar molecule involved. Fructose is generally found to be more reactive and selective toward HMF than glucose. Although these two sugar

molecules are isomers to each other and the same number of water molecules is lost during the HMF formation [6,11], it is not yet clear why there is a significant difference in their intrinsic reaction rate. Two main reaction pathways for their HMF conversions have been proposed in the literature [5,6]. The acyclic pathway proceeds via open chain intermediates such as 1,2-enediol and 3-deoxyglucos-2-ene common to both glucose and fructose [12,13]. The cyclic pathway on the other hand, proceeds via closed ring intermediates to HMF from fructose. Glucose conversion involves an extra isomerization step to fructose prior to HMF (Scheme 1) [14–19]. It has been claimed that catalysts with Lewis (LA) and/or Brønsted acid (BA) sites are needed for both sugar conversions, however there is no agreement among researchers which type and strength of acid are required. The mechanisms remain unclear regarding the two forms of sugars and their relationship [20,21]. In practice, sucrose, a dimer composed of glucose and fructose, is of main industrial interest because it is cheaper and more widely available than its components [22]. Although homogeneous acid catalysts, such as organic acids and ionic liquids, can give good yields and selectivities for sugar conversion, extensive product separation procedures make heterogeneous catalysts

* Corresponding author.

E-mail address: edman.tsang@chem.ox.ac.uk (S.C.E. Tsang).



Scheme 1. Dehydration pathways of glucose and fructose: acyclic pathway proposed by Anet et al. [13] and cyclic pathway proposed by Assary et al. [17]

more attractive. Similarly, separation difficulties are encountered with many yield-enhancing organic solvents employed to extract HMF from aqueous phase. Besides, the use of water as solvent is environmentally friendlier [5,7,8]. In order to make sucrose conversion scalable and sustainable we may need to consider its catalytic and process features in an industrial and environmental context. This requires an in-depth understanding of the underlying reaction mechanisms. However, the conversion of sucrose to HMF in comparison with glucose and fructose has not been investigated in depth yet. Our approach to this challenge is to carry out a systematic study of the conversion of glucose, fructose and sucrose to HMF in water over a variety of structurally related solid niobium oxides. Mechanistically, the conversion of sucrose is closely linked to that of its components glucose and fructose, making it worthwhile to study all three sugars comparatively. Niobium oxides are solid acids consisting of interconnected NbO_6 octahedra with varying extents of structural distortions and defects. Both BA and LA sites have been identified on niobium oxides, with acidic strength dependent on structure and environment, but the detailed relationship between structure and acidity is not clear [23–27]. In general, BA sites on metal oxides are associated with strongly acidic hydroxyl groups acting as proton donors and LA sites with exposed oxygen-deficient cations acting as electron pair acceptors [28–31]. Due to their strongly acidic character, niobium oxides have been studied previously for sugar conversion, for example, de Souza et al. obtained 28% HMF from glucose in

water over NbOH and Carlini et al. achieved 29% HMF from fructose in water over phosphoric acid treated NbOH [10,20]. However, the catalytic mechanisms have not been studied in detail in the aforesaid works, which could help to rationalize the reaction yields.

We are therefore interested in developing niobium oxide as a solid catalyst for the conversion of sucrose to HMF based on a deeper understanding of reaction mechanisms and catalytic features. Using TMP (trimethylphosphine) ^{31}P NMR we have been able to measure the acid properties of different niobium oxides more accurately than previous measurement techniques such as CO, pyridine FTIR and NH_3 TPD [32]. The detailed information obtained, in combination with structural analysis by Raman, TEM and XRD, enables us to gain new insights into how acidity correlates with structure in this compound group. Further, catalytic conversions over the niobium oxides for glucose, fructose and sucrose to HMF have been compared systematically. This offers some unique mechanistic insights into the sugar conversion, by correlating acid type and strength with fundamental reaction steps. We are able to demonstrate that mesoporous niobium oxide among all the different types of niobium oxide catalysts studied, gives the highest HMF yield from sucrose due to the balanced BA and LA sites of its structure with appropriate acidic strengths. Overall, we believe this study offers some new essential information, which will lead to a more rational design of solid acid catalysts for sugar conversion.

Download English Version:

<https://daneshyari.com/en/article/60645>

Download Persian Version:

<https://daneshyari.com/article/60645>

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