

## Short Communication

# Sustainable utilization of lignocellulose: Preparation of furan derivatives from carbohydrate biomass by bifunctional lignosulfonate-based catalysts

Dawei Chen <sup>a,b</sup>, Fengbing Liang <sup>a</sup>, Dexin Feng <sup>a,\*</sup>, Fanglin Du <sup>b</sup>, Guang Zhao <sup>a</sup>, Huizhou Liu <sup>a</sup>, Mo Xian <sup>a,\*</sup><sup>a</sup> CAS Key Laboratory of Biobased Materials, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, PR China<sup>b</sup> Key Laboratory of Nanostructured Materials, College of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, PR China

## ARTICLE INFO

## Article history:

Received 6 March 2016

Received in revised form 27 May 2016

Accepted 12 June 2016

Available online 14 June 2016

## Keywords:

Lignocellulose

Cellulose

Xylan

HMF

Furfural

## ABSTRACT

Bifunctional lignosulfonate-based catalysts (LS-M) with Lewis acid and basic sites were designed and prepared by immobilizing metal ions on lignosulfonate. Catalysts were characterized by XRD, XPS, SEM, EDX, TEM, TGA,  $\text{NH}_3/\text{CO}_2$ -TPD and FTIR, and applied in transformation of carbohydrate biomass to furan derivatives (HMF/furfural) in mixed water/THF systems. With LS-Cr as catalyst, the optimized yields of HMF from cellulose, glucose and mannose were 46.3%, 60.4% and 68.8%, and that of furfural from xylan, xylose and arabinose were 40.2%, 73.1% and 51.6%, respectively. The catalysts could be easily recycled with negligible wastage of the active metal ions.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Biofuels and biochemicals are considered as promising renewable and sustainable alternatives to our limited fossil resources, owing to their preparation using renewable biomass as raw materials [1–2]. Among all these compounds, furan derivatives (5-hydroxymethyl-furfural or furfural) converted from carbohydrate biomass are important platform chemicals for high value fuels, polymers and chemical intermediates [3–6].

Conversion of carbohydrate biomass has been investigated by the use of ionic liquids (ILs) as reaction medium with acid catalysts (mineral acid, metal halides, and solid acid catalysts) [3,6,7]. The ionic liquid–metal chloride has been confirmed as the best catalytic systems [8–9]. However, the process to produce HMF/furfural in ILs is expected to be costly due to the high cost and viscosity of ionic liquids, the extraction and purification of target products, and the catalysts [1]. In mixed water/organic solvent systems, heterogeneous acid catalysts show superior behavior over homogenous acids in terms of selectivity, recyclability and corrosion. Recently, a series of solid catalysts such as solid acid  $\text{SO}_4^{2-}/\text{SnO}_2$ , polymeric ILs (FPIL-Cr), alkaline earth phosphate ( $\alpha$ - $\text{Sr}(\text{PO}_3)_2$ ) were studied in transformation of cellulose to HMF with yields of 11.0%, 30.8%, and 34.0%, respectively [10–12]. Many

heterogeneous catalysts were also developed for the conversion of glucose/xylose to HMF/furfural with moderate yields (Table S1).

Lignosulfonate (LS) was usually used as an organic waste, surfactant or additive, which could be produced in abundance on the pulping cooking process [13–14]. Recently, LS catalysts with only Brønsted acid sites ( $\text{SO}_3\text{H}$  group) were developed as novel solid acids in catalysis fields, including esterification, Hantzsch and Strecker reactions, fructose/inulin-to-HMF or xylose-to-furfural transformation [15–18]. The stable structure and high thermal stability of LS, as well as the chelating property of sulfonic group with cationic species, provide the possibility for designing a new kind of lignosulfonate-based catalyst.

In this work, bifunctional lignosulfonate-based solid catalysts (LS-M) with Lewis acid and basic sites were prepared via a simple method by immobilizing metal ions [Cr(III), Sn(IV)] on LS. The resulting materials then were successfully applied in the conversion of cellulose/xylan and corresponding monose to furan derivatives (HMF/furfural) in mixed water/THF systems. A possible reaction mechanism was also deduced to insight the reaction process.

## 2. Experimental

## 2.1. Synthesis of lignosulfonate-based catalysts

Sodium lignosulfonate (Fig. S1, average molecular weight: 2000) was purchased from Aladdin Industrial Inc. (Shanghai). LS-M (M = Cr(III), Sn(IV)) catalysts were prepared by a coprecipitation method.

\* Corresponding authors.

E-mail addresses: [fengdx@qibebt.ac.cn](mailto:fengdx@qibebt.ac.cn) (D. Feng), [xianmo@qibebt.ac.cn](mailto:xianmo@qibebt.ac.cn) (M. Xian).

In a typical run of synthesis,  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}/\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  (10 mmol) and LS (20.0 g, 10 mmol) were dissolved in water (70 mL), and then heated at 80 °C for 4 h in a flask with magnetic stirring. The brown products were collected by centrifugation and rinsed with water and ethyl alcohol for 5 times, respectively, and then dried at 60 °C.

## 2.2. Catalyst characterization

Structural information and property of the LS-M catalysts were obtained by scanning electron microscopy with energy dispersive X-ray (SEM-EDX; Hitachi S-4800), transmission electron microscope (TEM; JEM-2000EX), powder X-ray diffraction (XRD; Bruker D8 Advance), X-ray photoelectron spectroscopy (XPS; Thermo ESCALAB 250XI), Fourier transform infrared spectroscopy (FTIR; Thermo Nicolet 8700), thermogravimetric analysis (TGA; Rubotherm-DynTHERM), and Temperature Programmed Desorption ( $\text{NH}_3/\text{CO}_2$ -TPD; Auto Chem II 2920). The contents of metal in LS-Cr (Cr: 35.53 wt%) and LS-Sn (Sn, 44.88 wt%) were estimated by EDX, respectively.

## 2.3. Catalytic conversion of carbohydrate biomass

Transformation reactions were performed in a 50 mL Teflon-line stainless steel autoclave. In a typical procedure, saccharides substrate (25 mg), catalyst (100 mg), THF (20 mL), water (10 mL) and NaCl (3.5 g) were added to the autoclaves. The reactant mixture was magnetically stirred at 500 rpm for a specific reaction time. The reaction was quenched by placing the reactor in an ice bath. The THF upper layer and the water sublayer were filtered and collected as samples for HPLC, respectively. The recycling experiments were carried out for five times. After each reaction, the catalyst was collected by centrifugation and used directly for the next run.

## 2.4. Analysis methods

The HMF and furfural were analyzed on HPLC (Waters 2489 equipped with Waters 1525 binary HPLC pump and ultraviolet detector). Content analyses of carbohydrate (glucose, fructose, xylose, mannose, arabinose) and organic acid (FA, AA, LA) were performed on Agilent 1200 series with an Aminex HPX-87H column and a refractive index (RI) detector. After reaction, the concentration of metal ion in water solution was determined by ICP-AES (IRIS Intrepid II XSP).

## 3. Results and discussion

### 3.1. Characterization of catalysts

The XRD patterns of the LS-Cr, LS-Sn and LS were illustrated in Fig. 1. Compared with LS, the XRD pattern of LS-Cr catalyst showed low crystallinity with one wide peak at  $2\theta$  of around 23°. The actual

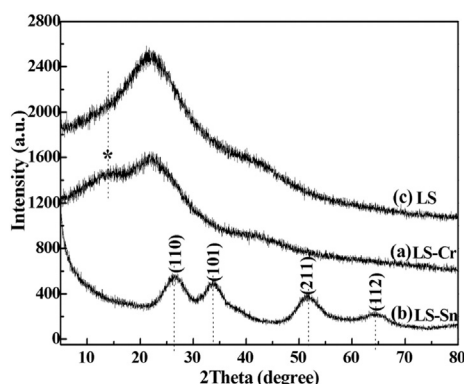


Fig. 1. XRD patterns of (a) LS-Cr, (b) LS-Sn and (c) LS.

compositions of LS-Cr was determined by the XPS spectrum of with photoelectron peaks located at 577 and 587 eV successively corresponding to the  $\text{Cr}2p_{3/2}$  and  $\text{Cr}2p_{1/2}$ , indicating the formation of  $\text{CrO}_x$ , as shown in Fig. 2. For LS-Sn, a range of diffraction peaks were assigned to the reflections of  $\text{SnO}_2$  crystalline structure (JCPDS 41-14445). The XPS peaks of LS-Sn(IV) located at 487 and 496 eV were also successively corresponding to the  $\text{Sn}3d_{5/2}$  and  $\text{Sn}3d_{3/2}$  ( $\text{SnO}_2$ ).

The FTIR spectras of LS-Cr, LS-Sn and LS were illustrated in Fig. S2. Compared with LS, the characteristic vibration bands at  $1597\text{ cm}^{-1}$  (the  $\text{O}=\text{S}=\text{O}$  symmetric stretching in  $\text{SO}_3\text{H}$ ) of LS-Cr and LS-Sn were decreased, indicating that the  $\text{SO}_3\text{H}$  groups exhibited good chelation activity with the Cr and Sn ion after the coprecipitation process.

The morphology of LS-Cr, LS-Sn and LS were characterized by SEM (Fig. 3) and TEM (Fig. S3), and the particle-size distribution of catalysts were measured and calculated. The LS showed a smooth surface and irregular flake morphology. However, the LS-Cr catalyst had microspheres-like structure with diameters ranging from 25 to 35 nm (calculated average: 30 nm). And meanwhile, the TEM image revealed that the particles of LS-Cr were overlapped each other in different degree. Differently, the average diameter of LS-Sn spheres was about 200 nm, and the spheres were composed of many particles of 20 nm in diameter. Interestingly, the TEM image presented that a core with diameter of about 5 nm existed in each LS-Sn particle.

The acidity and basicity of the catalysts were determined by  $\text{NH}_3$ -TPD and  $\text{CO}_2$ -TPD (Fig. S4), respectively. The contents of acidic sites (LS-Cr:  $1.2\text{ mmol g}^{-1}$ , LS-Sn:  $1.0\text{ mmol g}^{-1}$ ) were calculated. Compared with LS-Sn (basic sites:  $0.22\text{ mmol g}^{-1}$ ), LS-Cr (basic sites:  $0.19\text{ mmol g}^{-1}$ ) contained a stronger basicity peak. Furthermore, the thermogravimetric (TG) analysis revealed that LS-Cr and LS-Sn (Fig. S5) had good thermal robustness ( $<220\text{ }^\circ\text{C}$ ).

### 3.2. Performance of catalysts in carbohydrate biomass degradation to furan derivatives

The catalytic activities of the LS-M catalyst were examined using the degradation of cellulose in mixed water/THF systems. The optimized result on cellulose (25 mg) degradation was obtained at 190 °C for 8 h using LS-Cr as catalyst (100 mg, 6 mol% calculated by active Cr) in water/THF (1:2) systems. The highest HMF yield from cellulose was 46.3%, together with FA of 2.4%, AA of 0.2%, LA of 2.8%, and no furfural had been detected (Table 1, run 1).

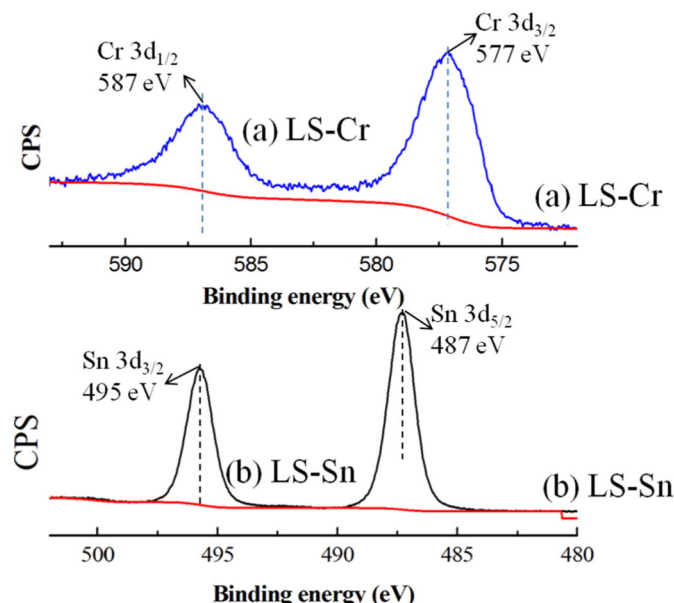


Fig. 2. XPS spectra of (a) LS-Cr and (b) LS-Sn.

Download English Version:

<https://daneshyari.com/en/article/6503319>

Download Persian Version:

<https://daneshyari.com/article/6503319>

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