Production of 5-Hydroxymethylfurfural from Fructose in Ionic Liquid Efficiently Catalyzed by Cr(III)-Al₂O₃ Catalyst

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A series of metal-Al₂O₃ catalysts were prepared simply by the conventional impregnation with Al₂O₃ and metal chlorides, which were applied to the dehydration of fructose to 5-hydroxymethylfurfural (HMF). An agreeable HMF yield of 93.1% was achieved from fructose at mild conditions (100 $^{\circ}$ C and 40 min) when employing Cr(III)-Al₂O₃ as catalyst in 1-butyl-3-methylimidazolium chloride ([Bmim]Cl). The Cr(III)-Al₂O₃ catalyst was characterized via XRD, DRS and Raman spectra and the results clarified the interaction between the Cr(III) and the alumina support. Meanwhile, the reaction solvents ([Bmim]Cl) collected after 1st reaction run and 5th reaction run were analyzed by ICP-OES and LC-ITMS and the results confirmed that no Cr(III) ion was dropped off from the alumina support during the fructose dehydration. Notably, Cr(III)-Al₂O₃ catalyst had an excellent catalytic performance for glucose and sucrose and the HMF yields were reached to 73.7% and 84.1% at 120 $^{\circ}$ C for 60 min, respectively. Furthermore, the system of Cr(III)-Al₂O₃ and [Bmim]Cl exhibited a constant stability and activity at 100 $^{\circ}$ C for 40 min and a favorable HMF yield was maintained after ten recycles.

Keywords 5-hydroxymethylfurfural, [Bmim]Cl, Cr(III)-Al₂O₃, fructose

Introduction

The irreversible consumption of the fossil fuels and the environmental problems have spurred the research of fuels and chemicals from biomass.^[1,2] In this context, 5-hydroxymethylfurfural (HMF), obtained by the catalytic dehydration of carbohydrates based on C₆ sugars, has been early envisaged as a versatile and promising intermediate.^[3] Either 2,5-diformylfuran (2,5-DFF)^[4] or 2,5-furandicarboxylic acid (2,5-FDCA)^[5] are produced by the selective oxidation of HMF. 2,5-FDCA is a desirable substitute for terephthalic or isophthalic acids in the fields of polyester production and a promising intermediate in the preparation of polyamides and polyurethane.^[6] Alternatively, levulinic acid synthesized by the hydrolysis of HMF can be converted into methyltetrahydrofuran (MTHF) and various levulinate esters, which can be used as additives in gasoline and biodiesel, respectively.^[7] However, the challenges have been posed to optimize the conversion process in an environmentally benign, economic and efficient way for the biomass into HMF.

From the previous researches, the preparation of HMF from carbohydrates has been conducted in aqueous media,^[8] organic solvents^[9] and ionic liquids (ILs).^[10] The utilization of water fulfills the principles of the green chemistry, but it shows unsatisfying selectivity

of HMF in the dehydration of carbohydrates, leading to many byproducts like levulinic acid and lactic acid. As reported by Yang et al., only a HMF yield of 22% was attained in water without combining tetrahydrofuran (THF) as extracting organic layer to protect HMF from further reactions with glucose.^[11] The organic solvents can suppress the unwanted side reactions and highlight the selectivity of HMF in the dehydration of hexose. However, higher activation energy may be necessary in such catalytic systems, thus, high temperature would be inevitable. According to the recent researches, 170 $\,^{\circ}C^{[12]}$ and 140 °C cooperated with microwaves^[13] were required to activate the catalytic systems in the solvents of butanol and DMSO, respectively. Meanwhile, the application of high boiling organic solvents increases the difficulty in the subsequent separation of HMF from the final products.

Consequently, the ILs appear to be a better choice. Zhao *et al.* first reported the Lewis acid catalyst (CrCl₂) could cooperate with the ionic liquid 1-ethyl-3-methyl-imidazolium chloride ([Emim]Cl) to achieve the HMF yield about 70%.^[14] And then many types of ILs have been attempted. Hu *et al.* studied the production of HMF from sucrose in 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF₄) using SnCl₄ as a catalyst and achieved a HMF yield of 65% at 120 °C for 24

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h.^[15] In subsequent studies, the conversion of fructose was also accomplished in [Emim]Cl with addition of $H_3PW_{12}O_{40}$ encapsulated in MIL-101 and HMF with high yield of 79% was attained at 80 °C for 2.5 h.^[9] Nearly 54% yield of HMF from glucose was achieved in a 50 : 50 (*w/w*) 1-hexyl-3-methylimidazolium chloride ([Hmim]Cl)-water mixture in the presence of ZrO₂ within 10 min at 200 °C.^[16] More recently, Yi *et al.* studied the dehydration of girasol, as a source of inulin, into HMF in 1-octyl-3-methylimidazolium chloride ([Omim]Cl) catalyzed by HCl at 120 °C for 1 h, and the yield of HMF was about 58.2%.^[17] However, high temperature and long reaction time may speed up the self- or cross-polymerization between fructose and generated HMF, demonstrating that HMF was no longer the favored product. Thus, the fructose dehydration to HMF based on mild reaction conditions should be explored.

In our previous work, ion-exchanged resins after acidification were employed as the catalyst, which achieved the fast conversion of fructose to HMF but failed in the conversion of glucose to HMF,^[18] possibly due to the fact that the acidic resins had a poor activity in the isomerization of glucose to fructose before the dehydration of fructose to HMF. Thus, besides focusing on an efficient conversion of fructose to HMF, the design and exploration of catalysts employed in this work were aiming at synthesis of HMF from more complex carbohydrates. In this context, the common Lewis acids, such as chromium halide, caught our eyes, due to their excellent activity in the dehydration of sugars into HMF even the substrate was rude biomass. Yi et al. reported that a yield of HMF about 60% was achieved from raw tapioca root biomass with high starch in [OMIM]Cl catalyzed by CrF_3 at 120 °C for 90 min.^[19] But the chromium ion is toxic and the separation of the Cr(III) or Cr(II) is still a problem. Fortunately, the heterogeneous catalysts have broadened the horizon of the study in sugar dehydration. Degirmenci et al. found that the catalyst of CrCl₂ supported on the mesoporous silica zeolite (CrCl₂-Im-SBA-15) highlighted the selectivity of HMF to 50% and realized the conversion to HMF from glucose in the aqueous medium.^[20] Furthermore, Zhang and Zhao revealed that a HMF yield of 40% was obtained from the dehydration of glucose under microwave irradiation in 2.5 min in the presence of hydroxyapatite supported chromium chloride (Cr-HAP).^[21] However, in the synthesis of CrCl₂-Im-SBA-15 and Cr-HAP, the high costs of CrCl₂ and hydroxyapatite (HPA) have posed the challenges on the industrialization and commercialization of these catalytic systems. Therefore, suitable support and the precursor of chromium are important for the preparation of supported chromium catalyst.

In recent years, aluminium oxide (Al₂O₃), as an abundant, cheap and commercially available material, has been widely used as the catalyst carrier in many organic reactions, such as reduction of NO_x ,^[22] reforming of methane^[23] and oxidation of CO_2 .^[24] And much

satisfying catalytic performance has been obtained. To the best of our knowledge, metal-Al₂O₃ catalysts were the first time used in the dehydration reaction from carbohydrates.

Herein, a series of metal-Al₂O₃ catalysts were prepared in the experiment, which were easily attained via the conventional impregnation with Al₂O₃ as the support in the aqueous metal chlorides solution. The metal chlorides included MgCl₂, ZnCl₂, MnCl₂, CrCl₃, WCl₆, MoCl₅, CuCl₂, FeCl₃, SnCl₄ and SnCl₂. And then these catalysts were applied to the dehydration of fructose to HMF. Additionally, the activity and stability of Cr(III)-Al₂O₃ in the sugar dehydration reaction and the optimum reaction conditions were investigated in our work. The aim was to study the effects of the introduction of metal ions into Al₂O₃ support on the dehydrating activity of sugar, thus exploring an optimal heterogeneous catalyst for the dehydration based on mild reaction conditions.

Experimental

Materials

HMF (99% purity) was purchased from Wutong Spice Co., Ltd. Chromium chloride hexahydrate (CrCl₃• 6H₂O, 99% purity), molybdenum chloride (MoCl₅, 99.6% purity) and tungsten chloride (WCl₆, 99.9% purity) were purchased from Aladdin. Fructose (B.R. grade), glucose (A.R. grade), sucrose (A.R. grade), maltose (B.R. grade), starch (A.R. grade), cellulose (column chromatography), aluminum oxide (Al₂O₃, A.R. grade), iron chloride (FeCl₃, A.R. grade), stannic chloride dihydrate (SnCl₂•2H₂O, A.R. grade), tin chloride pentahydrate (SnCl₄•5H₂O, A.R. grade), zinc chloride (ZnCl₂, A.R. grade), manganese chloride tetrahydrate (MnCl₂•4H₂O, A.R. grade), magnesium chloride hexahydrate (MgCl₂•6H₂O, A.R. grade), copper chloride dihydrate (CuCl₂•2H₂O, A.R. grade), barium sulfate (BaSO₄), ethyl acetate (CH₃COOC₂H₅, A.R. grade) and methanol alcohol (CH₃OH, L.C. grade) were purchased from Sinopharm Chemical Reagent Co., Ltd. 1-Butyl-3methylimidazolium chloride ([Bmim]Cl) was purchased from Shanghai Cheng Jie Chemical Co., Ltd. All of them were used as received without further purification.

Experimental methods

Preparation of the catalysts In a typical impregnation, Al_2O_3 was impregnated at 80 °C for 4 h in the aqueous solution of metal chlorides, including CrCl₃, FeCl₃, SnCl₂, SnCl₄, ZnCl₂, MnCl₂, MgCl₂, CuCl₂, WCl₆ and MoCl₅, and was dried at 80 °C overnight sequentially. Thus the supported metal- Al_2O_3 powder was obtained.

Characterization The X-ray diffraction (XRD) was recorded on a Bruker D8 diffractometer with Cu K α radiation (λ =1.54 Å) in the range of 2θ =10°-80°. The diffuse reflectance spectra (DRS) were measured by a UV-vis spectrometer (UV-2450, Shimadzu) in the

range of 200-800 nm. BaSO₄ was used as the reflectance standard material. Raman spectra were carried out at room temperature using a DXR Raman microscope with a 532 nm laser source. Temperature-programmed desorption of ammonia (NH₃-TPD) was performed on an apparatus TP-5079 (Tianjin Xianguan Limited Corporation). The pyridine adsorption infrared spectra (Py-IR) were recorded on a Perkin-Elmer Spectrum 2000. The pretreatment of samples in the NH₃-TPD analysis and the pyridine-absorbed FT-IR analysis were referred to literature.^[25] The metal content in solvent was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (VISTA-MPX, Varian, USA). The m/z parameters of samples were identified by liquid chromatography-linear ion trap mass spectrometer (LC-ITMS) (Thermo LXQ, USA).

Typical reaction procedure [Bmim]Cl (1.0 g) was preheated at the reaction temperature. Then, fructose (0.1 g) and the given amount of catalysts (metal-Al₂O₃) were charged into the [Bmim]Cl. Meanwhile, a magnetic stirrer started. After the desired time, the reaction mixture was cooled soon by an ice bath and diluted by pure water at the same time. The diluted solution was filtered before the HPLC analysis.

Analysis High performance liquid chromatography (HPLC) was employed to analyze the product. The HPLC setup was equipped with two Varian ProStar210 pumps, an Agilent TC-C (18) column, and a Varian ProStar325 UV-Vis Detector. 283 nm was the measured absorbance wavelength. The mobile phase was a solution of methanol and H₂O in the ratio 50 : 50 (V/V) at 0.8 mL/min flow rate. The temperature of column was kept at 35 °C by using a column oven. The yield of HMF was calculated as follows.

For fructose and glucose, HMF yield was defined as follows:

Yield =
$$\frac{n_{\rm HMF}}{n_{\rm monosaccharide}} \times 100\%$$

For disaccharides and polysaccharides, HMF yield was defined as follows:

$$\text{Yield} = \frac{n_{\text{HMF}}}{n_{\text{hexose-unites}}} \times 100\%$$

where n_{HMF} was the moles of HMF; $n_{\text{monosaccharide}}$ was the initial moles of fructose or glucose; $n_{\text{hexose-unites}}$ was the initial moles of hexose units in disaccharides or poly-saccharides.

Results and Discussion

Characterization of Cr(III)-Al₂O₃ catalyst

XRD patterns The XRD patterns, as presented in Figure S1, confirmed that the structure of Al_2O_3 in Cr(III)- Al_2O_3 catalyst was maintained. However, some redistribution of the XRD intensities in the catalyst took place compared with the pure Al_2O_3 material. Some changes at the angular values 2θ around 15° , 38° and 49° were attributed to the interaction of Cr(III) with the

Al₂O₃ frameworks and/or the changes in the symmetry of Cr(III) in the Al₂O₃ material.^[9,26] Diffraction peaks appeared at the angular values 2θ around 22° , 24° , 26° and 27° , which were ascribed to chromium oxide formed during the preparation of catalyst.

UV-vis analysis Figure S2 showed the UV-vis diffuse reflectance spectra of the catalysts. No absorption peak was observed for the alumina support in the 200– 800 nm region. Two absorption peaks at about 450 nm and 640 nm in the pure $CrCl_3 \cdot 6H_2O$ were found, which were assigned to the absorption of Cr(III).^[27] In addition, it was observed that the maximum absorption band of Cr(III) was shifted to longer wavelength in the Cr(III)- Al_2O_3 catalyst, indicating that some Cr(III) interacted with the Al_2O_3 support in the impregnation.

FT-Raman spectroscopy The Raman spectra of different samples were presented in Figure 1. Any Raman feature in the alumina support was not found in the $200-1200 \text{ cm}^{-1}$ region, therefore, all the observed Raman bands in other samples were assigned to chromium species vibrations. In the spectra of CrCl₃•6H₂O, three bands at around 261, 324 and 460 cm⁻¹ were observed. which were attributed to the water librations and the Cr-Cl stretching.^[28] After loading CrCl₃ on Al₂O₃ carrier to form Cr(III)-Al₂O₃ catalyst, these bands all shifted to lower wave number. What's more, a small and sharp Raman band at around 362 cm⁻¹ was found in the spectra of Cr(III)-Al₂O₃ catalyst, which was attributed to Cr-O bending modes.^[29] It was proved that the interaction between the Cr(III) and the alumina support was formed. Moreover, a band at 539 cm^{-1} belonged to the formation of crystalline Cr_2O_3 was also observed in Cr(III)-Al₂O₃ catalyst,^[29,30] which was consistent with the result of the XRD patterns. But the band was broader than that reported in the literature, maybe due to the overlap with the band at 453 cm^{-1} .

NH₃-TPD analysis The temperature programmed desorption of ammonia was measured to characterize the acidity of the Cr(III)-Al₂O₃ catalyst. Figure 2 showed the NH₃-TPD profiles of different samples and the results were summarized in Table 1. Two NH₃ desorption peaks at 272 and 549 °C were observed in the



Figure 1 Raman spectra of different samples: (a) Al_2O_3 , (b) Cr(III)- Al_2O_3 , (c) $CrCl_3$ • $6H_2O$.

profile of Al₂O₃, which were attributed to weak acid site and strong acid site on the surface of Al₂O₃, respectively.^[31] After supporting Cr³⁺, the higher-temperature desorption peak areas decreased significantly and the peak temperature shifted to lower temperature, showing the weakening of strong acidity. Meanwhile, the desorption peak at low-temperature shifted to higher temperature and new peaks were found, indicating the increase of weak acidity. A new desorption peak at 379 °C in the profiles of Cr(III)-Al₂O₃ was found, which belonged to the moderate acid site. The results indicated that the addition of Cr changed the acidity of catalyst. Moreover, it could be found in Table 1 that the total acidity from the Cr(III)-Al₂O₃ catalyst was on a rise with modification of Cr. It showed that the Cr incorporation indeed created more acidic sites in the aluminum framework. But it was interesting that the acid strength distribution of Cr(III)-Al₂O₃ was uniform among the weak, moderate and strong acidity in comparison with aluminum support from the data in Table 1.

Pyridine-adsorbed FT-IR analysis The type of acid on Cr(III)-Al₂O₃ catalyst was determined by pyridine adsorption infrared spectroscopy and the result was illustrated in Figure 3. Four major bands at 1447, 1488, 1537 and 1587 cm^{-1} were found in the spectroscopy of Cr(III)-Al₂O₃ catalyst. While referring from the reports of Wang et al., the bands at about 1450 and 1540 cm⁻ were assigned to Lewis acidic site and Brønsted acidic site, respectively, and the band at 1490 cm⁻¹ was characteristic of pyridine adsorbed on both Lewis and Brønsted acid sites.^[25] The results proved that Cr(III)-Al₂O₃ catalyst contained two kinds of acidity sites: Lewis and Brønsted acidity sites. Comparing the spectra of Cr(III)-Al₂O₃ catalyst with that of Al₂O₃, the intensity and peak area of the band at about 1450 cm⁻¹ increased, which indicated that the Lewis acidity of Cr(III)-Al₂O₃ might



Figure 2 NH₃-TPD profiles of Al₂O₃ and Cr(III)-Al₂O₃ catalyst.

come from Al_2O_3 and the immobilized chromium ion. In addition, it was reported that the chromium ion might coordinate with the alcohol group and the oxygen atom on the surface of Al_2O_3 through the impregnation, leading to initiating some Brønsted acidity for the Cr(III)- Al_2O_3 catalyst.^[32]



Figure 3 FT-IR pyridine adsorption spectra of Al_2O_3 and Cr(III)- Al_2O_3 catalyst.

Sugar dehydration reactions and recycle experiments

Effects of metal chlorides Initially, the effects of different metal ions supported on Al₂O₃ on the conversion of fructose to HMF were explored and the results were shown in Figure 4. In the blank experiment (without loading any metal ion on the Al₂O₃), the HMF yield was quite low, indicating that the catalytic activity for the dehydration of fructose from the catalyst carrier (Al₂O₃) was negligible. As shown in Figure 4, different HMF yields, ranging from 4.2% to 84.3%, were observed after supporting different metal ions on Al₂O₃. It illustrated that the catalytic activities of metal-Al₂O₃ catalysts were depended on the properties of metal ions largely. An excellent yield of 84.3% was achieved when Cr(III)-Al₂O₃ was employed. Only moderate yields were obtained with the Sn(IV)-Al₂O₃, Cu(II)-Al₂O₃, W(VI)-Al₂O₃ and Mo(V)-Al₂O₃ catalysts and even low vields were reached with the Fe(III)-Al₂O₃ and Sn(II)-Al₂O₃ catalysts. However, not all the metal ions supported on Al₂O₃ were effective, the modification of Al₂O₃ with Zn(II), Mn(II) and Mg(II) did not trigger the conversion of fructose to HMF, respectively.

Recognizing that the dehydration of fructose to HMF was an acid-catalyzed process, therefore, it became more easily with the increasing of the acidity of the catalytic metal centers. According to the researches of

Table 1	The acid strength distribution	of the catalysts calculated by	y the results of NH ₃ -TPD profiles
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Sample	Total acidity/ (mmol NH ₃ /g)	Weak acidity/ (mmol NH ₃ /g)	Temp./°C	Moderate acidity/ (mmol NH ₃ /g)	Temp./°C	Strong acidity/ (mmol NH ₃ /g)	Temp./°C
Al ₂ O ₃	0.87	0.09	272	—	—	0.78	549
Cr(III)-Al ₂ O ₃	1.35	0.38	282	0.57	379	0.40	501

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Figure 4 The fructose dehydration to HMF catalyzed by different metal-Al₂O₃ catalysts.

Zhang *et al.*, Cr(III) showed the stronger Lewis acidity in comparison with other metal cations,^[33] possibly accelerating the dehydration of fructose. Thus, Cr(III)-Al₂O₃ catalyst was selected as the optimum catalyst in the subsequent experiments.

To investigate the effect of metal ion and the carrier on the dehydration of fructose, some controlled experiments were carried out and the results were shown in Table 2. Obviously, only HMF yield of 4.3% was obtained when 0.1 g Al₂O₃ (entry 3) was used as catalyst due to the low Lewis acidity of Al₂O₃. HMF yield boosted to 74.9% when 0.1 g CrCl₃ (entry 2) was applied, possibly resulting from that CrCl₃ owned stronger acidity and new catalyst ([Bmim]CrCl₄) could be formed by the interaction between CrCl₃ and [Bmim]Cl.^[34] However according to the proportion of CrCl₃ and Al₂O₃ in supported Cr(III)-Al₂O₃ catalyst, directly adding 0.1 g mixture of CrCl₃ and Al₂O₃ (entry 4) in the system as catalyst, HMF yield slightly decreased in comparison with entry 2. It might be due to the decrease of CrCl₃ dosage and the hindrance effect of Al_2O_3 for the mass transfer process.

Table 2The effects of different catalysts on the dehydration of
fructose a

Entry	Catalyst	HMF yield/%
1	Cr(III)-Al ₂ O ₃	84.3
2	CrCl ₃	74.9
3	Al ₂ O ₃	4.3
4	CrCl ₃ +Al ₂ O ₃	67.6

 a Conditions: catalyst 0.1 g, fructose 0.1 g, [Bmim]Cl 1.0 g, 90 °C, 40 min.

Furthermore, it was noteworthy that the Cr(III)- Al_2O_3 catalyst (entry 1) prepared by impregnation method showed the highest dehydration activity and HMF yield reached to 84.3%. It clearly indicated that the distributed loading of Cr(III) ion on Al_2O_3 carrier by the impregnation method facilitated the dehydration of fructose and the formation of HMF. It was possibly arisen from that more acidic sites in the aluminum

framework were created by immobilization of Cr, which was in accordance with the result of NH₃-TPD profiles. In addition, the result was due to that part of Cr(III) ions could be distributed on surface of Al₂O₃ carrier and the others might be entered into the channel of Al₂O₃ or exchanged into the framework of Al_2O_3 through the impregnation method,^[25,35] which was consistent with the result of UV-vis diffuse reflectance spectra and Raman spectra. Therefore, as shown in Figure 5, fructose could react with not only the Cr(III) ion on the surface of Al₂O₃ carrier but also those in the porous channel in the conversion of fructose to HMF. Thus, the HMF generated in the porous channel of the Al₂O₃ carrier, might be inhibited from further self- and cross-polymerization with fructose. Furthermore, the pyridine-adsorbed FT-IR spectrum demonstrated the existence of two types of acid sites on the Cr(III)-Al₂O₃ catalyst, favoring the dehydration of fructose to HMF.^[36]



Figure 5 The schematic diagram for fructose dehydration to HMF on Cr(III)-Al₂O₃ catalyst.

However, a question arose whether Cr(III) ion was able to drop off from the Al₂O₃ support during the reaction. The results listed in Table 2 did not satisfactorily confirm that the actual activity center for the fructose dehydration was the Cr(III) ion distributed on Al₂O₃ rather than the dissociative Cr(III) ion dropped from the Cr(III)-Al₂O₃ catalyst. It was reported that the dissociative Cr(III) ion could react with [Bmim]Cl to form [Bmim]CrCl₄ like Fe(III) ion^[37] at such reaction conditions (100 $^{\circ}$ C and 40 min). Therefore, according to the literature,^[38] [Bmim]CrCl₄ was prepared by mixing [Bmim]Cl and CrCl₃, and the reaction solvents after 1st reaction run and 5th reaction run were collected through filtration, respectively. Meanwhile, a control experiment was conducted by mixing [Bmim]Cl and CrCl₃ at 100 °C for 40 min in order to test that whether [Bmim]CrCl₄ could be formed at such reaction conditions. Two characterizations including ICP-OES and LC-ITMS were further employed to characterize these samples. Firstly, the reaction solvents were detected by ICP-OES and no Cr(III) ion was traced in both of them. Secondly, all samples were characterized by LC-ITMS method and the results were shown in Figure 6. It was confirmed that [Bmim]⁺ cation existed in all of samples from the result of Figure 6a and the reaction conditions (100 °C and 40 min) were enough to form $CrCl_4$ by

comparing Figure 6b-1 with Figure 6b-2. But no molecular ion peak of $CrCl_4^-$ was found in both of Figure 6b-3 and Figure 6b-4, indicating that no $CrCl_4^-$ was formed during the dehydration. The results indicated that the Cr(III) ion preferred to be loaded on the carrier Al_2O_3 rather than be dropped off during the dehydration in the ionic liquid [Bmim]Cl, although the Cr(III) ion had strong dispersibility in the aqueous media.



Figure 6 LC-ITMS spectra of the cations (a) and anions (b) in all of samples: (a-1 and b-1) [Bmim]CrCl₄ prepared by the method reported in the literature, (a-2 and b-2) the mixture of [Bmim]Cl and CrCl₃, (a-3 and b-3) reaction solvent after 1^{st} reaction run and (a-4 and b-4) reaction solvent after 5^{th} reaction run.

Effects of catalyst dosage The effects of different catalyst dosages on the HMF yields were examined and the results were shown in Table 3. As seen in Table 3, HMF yields first increased and then decreased with the increasing dosages of catalyst. The HMF yield was only 5.3% in control experiment, however, the yield of HMF boosted to 76.1% when 0.025 g Cr(III)-Al₂O₃ was added. The result confirmed the excellent catalytic performance of Cr(III)-Al₂O₃ in this dehydration reaction. As shown in Table 3, the yield of HMF maximized to 87.7% when increasing the catalyst dosage to 0.075 g. The reason might be that the kinetics of fructose dehydration was faster with the increase of catalytic sites provided by more catalyst dosage in the reaction. However, the HMF yields decreased smoothly when the amount of catalyst was increased from 0.075 to 0.150 g and then remained unchanged with the further increase of catalyst dosage. The results might be ascribed to that the side reactions in the catalytic system were also accelerated by the over-using catalysts. Thus, the dosage of Cr(III)-Al₂O₃ was chosen as 0.075 g in the subsequent experiments.

Table 3 The effects of the dosages of Cr(III)- Al_2O_3 on the dehydration of fructose^{*a*}

Entry	Cr(III)-Al ₂ O ₃ /g	HMF yield/%	
1	0	5.3	
2	0.025	76.1	
3	0.050	81.5	
4	0.075	87.7	
5	0.100	84.3	
6	0.150	80.8	
7	0.200	80.8	

^a Conditions: fructose 0.1 g, [Bmim]Cl 1.0 g, 90 °C, 40 min.

Effects of reaction temperature and time Figure 7 showed the influence of the reaction temperature on the dehydration of fructose to HMF. Obviously, the initial yields of HMF were on the rise with the elevation of the temperature. More precisely, the high temperature shortened the time to reach the maximum value of HMF yields. HMF yield of 93.1% was obtained at 100 $^{\circ}$ C for 40 min, while it only took 20 and 5 min to reach HMF yield of 91.2% at 110 $^{\circ}$ C and 91.3% at 120 $^{\circ}$ C, respectively. The results indicated that high temperature may speed up the dehydration of fructose.



Figure 7 HMF yield as a function of the reaction time at different temperatures.

Moreover, the change of HMF yields was found at different temperatures with the prolonging of reaction time in Figure 7. HMF yields increased quickly in the first 40 min at lower temperature (80 and 90 $^{\circ}$ C) and the lower the temperature was, the more apparent the tendency was. In the following 20 min, the rise of HMF yield became smoothly. It showed that at lower temperature the prolonging of reaction time could highlight HMF yields effectively. When raising the temperature to

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100 and 110 °C, HMF yields increased firstly and then decreased with extending the reaction time. It was reported that some side reactions occurred in the process of the dehydration of fructose, resulting in forming some insoluble humins and soluble polymers by the self- and cross-polymerization of HMF.^[13] Furthermore, with the formation of H₂O in the process of the dehydration inevitably, the alternation of the solvent from [Bmim]Cl to [Bmim]Cl/H₂O mixture solvent gave the chance to the rehydration of the HMF, leading to the generation of levulinic acid.^[39] Therefore, high temperature might accelerate not only the dehydration reaction to HMF, but also some undesirable side reaction, demonstrating that HMF was no longer the favored product. When reaction temperature was further increased (120 °C), the HMF yield reached the maximum in the first 5 min, and then declined continuously with the extension of time, which confirmed the conclusion again. Thus, 100 °C and 40 min were considered as the optimized reaction temperature and time, respectively.

Effects of initial fructose concentration The effects of the initial concentration of fructose on HMF vields in [Bmim]Cl were illustrated in Table 4. HMF yield decreased continuously with the increase of initial concentration of fructose. High HMF yield was observed at the extremely low concentration of fructose (4.8 wt%) in ILs. When the concentration of fructose increased to 9.1 wt%, the HMF yield decreased slightly to 93.1%. Further increasing the initial concentration of fructose to 16.7 wt%, an obvious change of HMF yield was observed. As discussed above, the result could be ascribed to the polymerization of HMF and fructose to form humins.^[13] However, additional increase of the fructose did not lead to a significant decline of the HMF yield in the ensuing process. When the initial concentration of fructose increased to 23.1 wt%, HMF yield only decreased to 84.1%. The reason might be due to the existence of [Bmim]Cl, as a benign catalytic media in the biomass dehydration, retarding the formation of unwanted side products. An HMF yield of 82.5% was still achieved with the initial fructose concentration of 28.6 wt% (0.4 g) at 100 °C for 40 min, indicating that the Cr(III)-Al₂O₃/[Bmim]Cl system owned a high catalytic efficiency for this dehydration reaction.

Table 4 The influence of different initial fructose loadings onthe yield of the reaction^a

Entry	Initial fructose concentration/wt%	Initial fructose loading/g	HMF yield/%
1	4.8	0.05	96.0
2	9.1	0.10	93.1
3	16.7	0.20	85.9
4	23.1	0.30	84.1
5	28.6	0.40	82.5

^{*a*} Conditions: Cr(III)-Al₂O₃ 0.075 g, [Bmim]Cl 1.0 g, 100 $^{\circ}$ C, 40 min.

Conversion of different substrates to HMF with Cr(III)-Al₂O₃ catalyst In general, a one-pot synthesis of HMF from disaccharide and polysaccharide was more complicated than fructose and the hydrolysis, isomerization and dehydration reactions would take place one by one in the process, resulting in the difficulty in the conversion of biomasses to HMF. Therefore, to evaluate the scope of application of Cr(III)-Al₂O₃ catalyst, monosaccharide (fructose and glucose), disaccharide (sucrose and maltose) and polysaccharide (starch and cellulose) were selected as substrates in the experiment and the results were exhibited in Table 5.

As shown in Table 5, Cr(III)-Al₂O₃ catalyst showed a favorable catalytic activity for glucose and sucrose besides fructose, attributed to the fact that Cr(III)-Al₂O₃ catalyst contained two types of acid sites (Lewis and Brønsted acid sites). The hydrolysis of sucrose and the isomerization of glucose into fructose were catalyzed more easily by Lewis acid, whereas Brønsted acid favored the dehydration of fructose into HMF.^[36,40] Un-fortunately, the yields of HMF from starch and cellulose were quite poor under the same reaction conditions, possibly due to the complicacy in the hydrolysis of these macromolecules.

 Table 5
 The influence of different sugars on the yield of the reaction

Entry	Sugar	HMF yield/%	
1 ^{<i>a</i>}	Fructose	91.3	
2^b	Glucose	73.7	
3 ^{<i>b</i>}	Sucrose	84.1	
4^b	Maltose	48.3	
5^b	Starch	23.3	
6^b	Cellulose	12.2	

^{*a*} Conditions: Cr(III)-Al₂O₃ 0.075 g, sugar 0.1 g, [Bmim]Cl 1.0 g, 120 °C, 5 min. ^{*b*} Conditions: Cr(III)-Al₂O₃ 0.075 g, sugar 0.1 g, [Bmim]Cl 1.0 g, 120 °C, 60 min.

Recycling of [Bmim]Cl and Cr(III)-Al₂O₃ catalyst Long-term reusability was of great significance for employing a catalyst in industrial process. In this work, the reuse of Cr(III)-Al₂O₃ catalyst and the [Bmim]Cl was carried out to investigate the stability and activity of catalyst. 1 mL of pure water should be added into the reaction mixture after the 1st run in order to decrease the viscosity of [Bmim]Cl and facilitate the extraction of HMF. After the extraction of HMF by ethyl acetate, the mixture was heated at 60 °C for 24 h, aiming to remove the residual water and ethyl acetate after extraction. The extracted liquid was examined by UV-Vis detector in an external standard to attain the amount of HMF. Then the dried [Bmim]Cl solvent with Cr(III)-Al₂O₃ catalyst was utilized directly in the next run by adding 0.1 g fructose under the same reaction conditions. As shown in Figure 8, the decrease of the catalytic activity was negligible after 10th run, which demonstrated that the Cr(III)-Al₂O₃ catalyst exhibited an excellent stability for the fructose dehydration into HMF. Surprisingly, the HMF yields in some recycling tests were even higher than that in the 1st run, but the change range was very slight, which might be due to the acceptable experimental error.



Figure 8 Recycle of IL and Cr(III)-Al₂O₃ catalyst.

Conclusions

In summary, a series of metal-Al₂O₃ catalysts were prepared easily via conventional impregnation method. By screening different metal-Al₂O₃ catalysts, it was demonstrated that Cr(III)-Al₂O₃ and [Bmim]Cl were an excellent combination for the conversion of fructose into HMF and a satisfactory HMF yield of 93.1% was achieved at mild conditions (100 °C, 40 min). The Cr(III)-Al₂O₃ catalyst was characterized via XRD, DRS and Raman spectra to clarify the interaction between the Cr(III) and the alumina support. Meanwhile, the reaction solvents after 1st reaction run and 5th reaction run were collected through filtration and analyzed by ICP-OES and LC-ITMS, which confirmed that no Cr(III) ion was dropped off from the alumina support during the dehydration of fructose. Furthermore, visible results were also obtained when glucose, sucrose, maltose, starch and cellulose were as the feedstock. Notably, a favorable catalytic activity was observed in Cr(III)-Al₂O₃/[Bmim]Cl system for the glucose and sucrose and the HMF yields reached to 73.7% and 84.1% at 120 \degree C for 60 min, respectively. Meanwhile, the system with Cr(III)-Al₂O₃ as catalyst and [Bmim]Cl as solvent can be efficiently reused and the catalytic activity retained steadily after 10 times recycling. Hence, the Cr(III)-Al₂O₃ and [Bmim]Cl catalytic system has an excellent potential in the synthesis of HMF from biomass for its high efficiency, reusability and low price.

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