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Article

Efficient production of 5-hydroxymethylfurfural from hexoses using solid acid $\text{SO}_4^{2-}/\text{In}_2\text{O}_3$ -ATP in a biphasic system

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ARTICLE INFO

Article history:

Received 19 February 2016

Accepted 25 March 2016

Published 5 August 2016

Keywords:

Solid acid catalyst

Attapulgite

5-Hydroxymethylfurfural

Biphasic system

Fructose dehydration

Glucose isomerization

ABSTRACT

A natural attapulgite (ATP)-based catalyst, sulfated In_2O_3 -ATP ($\text{SO}_4^{2-}/\text{In}_2\text{O}_3$ -ATP), was obtained by an impregnation-calcination method and was used to efficiently and selectively produce the useful platform chemical 5-hydroxymethylfurfural (HMF) from hexoses. Some important reaction parameters were studied, revealing that Lewis and Brønsted acid sites on $\text{SO}_4^{2-}/\text{In}_2\text{O}_3$ -ATP catalyze glucose isomerization and fructose dehydration. The yields of HMF from glucose and fructose were 40.2% and 46.2%, respectively, using the optimal conditions of 180 °C for 60 min with 10 wt% of solid acid catalyst in a mixture of γ -valerolactone-water (9:1).

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1. Introduction

Biorefineries are regarded as an alternative to use fossil resources to provide useful chemicals. Developing biorefineries has attracted growing interest because fossil resources are being depleted and are the cause of environmental concerns [1–3]. In the same way that petroleum refineries produce chemicals that are the building blocks for more complex molecules such as polymers, biorefineries will manufacture simple molecules from readily available feedstocks to allow the synthesis of biopolymers and other large molecules [4]. One approach that has been broadly studied is the production of furans from carbohydrates. 5-Hydroxymethylfurfural (HMF), a dehydration product of hexose, is one of the most important

platform chemicals [5,6] because of its potential to substitute petroleum-derived building blocks for the production of polyamides and fine products [7–9]. Developing an efficient catalytic system for the dehydration of carbohydrates to HMF has become a hot topic.

Heterogeneous catalysts such as zirconium phosphate, niobic acid, aluminosilicate, alumina and zeolites [10–13] have been investigated for the selective and catalytic conversion of carbohydrates into HMF, with promising results. Qi et al. [14] explored the dehydration of fructose to HMF with sulfated zirconia under mild conditions and achieved a yield of 72.8% in acetone-dimethylsulfoxide mixtures. Furthermore, Wang et al. [15] reported HMF preparation from fructose in 75.0% yield using a solid acid catalyst (sulfated SnO_2 - ZrO_2) in DMSO at 120

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This work was supported by the Fundamental Research Funds for the Central Universities (TD2011-11, BLYJ201519), Beijing Higher Education Young Elite Teacher Project (YETP0765), National Natural Science Foundation of China (31170556), New Century Excellent Talents in University (NCET-13-0671), and State Forestry Administration of China (201204803).

DOI: 10.1016/S1872-2067(15)61096-8 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 8, August 2016

°C for 2.5 h. Unlike conventional soluble acid catalysts or metal chlorides, insoluble acids can adjust the surface acidity of the catalytic particles to improve the selectivity for HMF [16]. Furthermore, clay-based heterogeneous catalysts have many practical and potential applications as green catalysts. Another potential catalyst is attapulgite (ATP), a hydrated octahedral layered magnesium aluminum phyllosilicate $[(\text{Mg}, \text{Al})_4(\text{Si})_8(\text{O}, \text{OH}, \text{H}_2\text{O})_{26} \cdot n\text{H}_2\text{O}]$. ATP is a low-cost mineral with a fibrous morphology of which China has large reserves [17,18]. To the best of our knowledge, there are few reports of the use of natural clay particles in the conversion of carbohydrates to HMF.

γ -Valerolactone (GVL) is a valuable product that can be produced at a yield greater than 95% through hydrogenation of levulinic acid (LA) derived from HMF. GVL may be blended with gasoline in a capacity similar to ethanol or used to make organic solvents, chemicals, transportation fuels, valeric esters, and butene isomers [19–22]. Dumesic's group [23] designed a biphasic reaction system using GVL as a solvent and a combination of Amb-70 and Sn- β as a solid acid catalyst to convert glucose to HMF in up to 59% yield.

InCl_3 has emerged as an easily-handled and eco-friendly Lewis acid catalyst. In(III) catalysts have been previously shown to enhance the conversion of cellulose to HMF [25,26]. We propose a new solid acid In(III) catalyst, $\text{SO}_4^{2-}/\text{In}_2\text{O}_3\text{-ATP}$, using GVL as the solvent to prepare HMF from hexoses (Scheme 1). Herein, we report the preparation of catalysts by an impregnation-calcination method using ATP powder with indium as a metal precursor and investigate the selectivity and efficiency of the conversion of hexoses (glucose and fructose) to HMF. The effects of different ATP-based catalysts, reaction temperature, reaction time and acid concentration were investigated in detail.

2. Experimental

2.1. Reagents

Glucose (99%), D-fructose (99%), H_2SO_4 (95%–98%), and $(\text{NH}_4)_2\text{SO}_4$ (99%) were purchased from Sinopharm Chemical Reagent Co., Ltd (Beijing, China) and used without further purification. Indium (99.99%) was purchased from Xiya Reagent (Shandong, China). GVL (98%) was obtained from Adamas Reagent Co., Ltd (Shanghai, China). HMF (98%) and levulinic acid (98%) were supplied by Acros Organics.

2.2. Preparation of solid acid $\text{SO}_4^{2-}/\text{In}_2\text{O}_3\text{-ATP}$

$\text{SO}_4^{2-}/\text{In}_2\text{O}_3\text{-ATP}$ was prepared by an impregnation-calcination method. ATP powder (50 g) was placed in a 500-mL beaker containing concentrated H_2SO_4 (15 mL) and Indium (2 g).

The powders were dispersed on a shaker, $(\text{NH}_4)_2\text{SO}_4$ solution (60 mL, 1 mol/L, equal to 40 g of $(\text{NH}_4)_2\text{SO}_4$) was added and the dispersion shaken violently for 180 min. The resulting gray solid was isolated by filtration and further calcined at 550 °C for 120 min. The calcined solid was immersed in concentrated sulfuric acid solution for 120 min. The solid was isolated by filtration and heated at 400 °C for 120 min. The resulting white powder was ground and sieved (100 mesh) to give $\text{SO}_4^{2-}/\text{In}_2\text{O}_3\text{-ATP}$, designated as SIA hereafter. Two alternative preparations of the catalyst were undertaken in the absence of indium and omitting the calcination step are signified as SA and n-SIA, respectively.

2.3. Catalyst characterization

A scanning electron microscope (SEM, SU8010; Hitachi) and transmission electron microscope (TEM, HT7700; Hitachi) were used to identify the morphology of the catalysts. X-ray photoelectron spectroscopy (XPS) was performed using an Axis Ultra spectrometer (Kratos Analytical, UK) with a monochromated Al K_{α} source. The X-ray diffraction (XRD) patterns of the catalysts were collected using a Bruker D8 Advance X-ray diffractometer (Cu $K_{\alpha 1}$ irradiation). The pore structures were characterized on a Micromeritics ASAP 2010 gas adsorption analyzer by N_2 adsorption-desorption isotherms at liquid N_2 temperature. Samples were degassed at 200 °C for 2 h under vacuum before measurements were taken. The average pore diameter was calculated using the Barrett-Joyner-Halenda method based on the desorption isotherm, and surface area was calculated by using the Brunauer-Emmett-Teller adsorption isotherm method.

The Brönsted and Lewis acid sites of the samples were determined using a TENSOR27 FT-IR spectrometer (Bruker) in a quartz cell equipped with CaF_2 windows. Samples (15 mg) were pressed into self-supporting wafers and then placed in the cell. Each sample was preheated at 400 °C under a vacuum of 1×10^{-2} Pa for 2 h to remove water, followed by pyridine (Py) vapor adsorption for 10 min at room temperature. Pyridine was removed by degassing under vacuum for 30 min at specific desorption temperatures (150 and 400 °C) prior to recording the FT-IR spectra.

2.4. General procedure for the synthesis of HMF and analysis of the products

A glucose or fructose solution (30 g, 2 wt%) was added into an autoclave (50 mL) at a range of temperatures for set periods of time. An acid concentration of 10 wt% SIA was used for aqueous systems. Biphasic systems consisted of GVL and an aqueous suspension containing the catalysts. At the end of the

Scheme 1. Reaction scheme for the production of HMF from hexose.

reaction, aqueous samples were collected, filtered through a 0.2-mm filter and analyzed by HPLC (Agilent 1260 system with a Bio-Rad Aminex HPX-87H column and an RI detector). The organic layer of the biphasic reactions was diluted (0.1 mL diluted in 1 mL of distilled water) and then filtered through a 0.2-mm filter prior to HPLC analysis. The conversion of the hexoses (X), yield of the products (Y) and selectivity for the products (S) were evaluated on a carbon basis using the following equations: $X = (\text{moles of glucose remaining}/\text{moles of starting amount of glucose}) \times 100\%$, $Y = (\text{moles of HMF or LA}/\text{moles of starting amount of glucose}) \times 100\%$, $S = (Y/X) \times 100\%$.

3. Results and discussion

3.1. Catalyst characterization

The SEM images of ATP, SA, n-SIA, and SIA are shown in Fig. 1. The catalysts were found to form fibers with an average length of about 60 nm. Regular, smooth surfaces were present on n-SIA and ATP crystals, whereas tight, rough surfaces were formed on SA and SIA during the calcination process at 550 °C. The surface of SIA was also covered with many smaller particles, which are likely present because of the immersion in H_2SO_4 solution and the introduction of indium [15]. The catalysts were next examined by TEM. Bundles of multiple ATP fibers were obtained after calcination at high temperature (Fig. 2(b) and (d)), which could result from aggregation of partial metal oxide particles [24].

FT-IR spectroscopy of the catalyst with chemisorbed pyridine (Py-IR) was used to distinguish the Brönsted and Lewis acid sites on the samples. Fig. 3 displays the Py-IR spectra of SA and SIA between 1300 and 1700 cm^{-1} . The peaks at 1447 and 1449 cm^{-1} are assigned to pyridine adsorbed to Lewis acid sites, the peak at 1543 cm^{-1} characterizes pyridine adsorbed to

Fig. 3. Py-IR spectra of SA (1) and SIA (2).

Brönsted acid sites, while the peak at 1490 cm^{-1} indicates pyridine adsorbed to both Brönsted and Lewis acid sites simultaneously. The Brönsted and Lewis acid sites on $\text{SO}_4^{2-}/\text{In}_2\text{O}_3$ -ATP catalyze glucose isomerization and fructose dehydration, respectively. The Py-IR spectra show that the number of acid sites on SIA was much larger than that of the ATP carrier. Fig. 4 shows the XPS measurements for SA and SIA, and the magnified signals attributed to S 2p and In 3d. Both SA and SIA clearly exhibited Mg, Al and Si signals, indicating the presence of ATP. SIA also exhibited signals from In 3d, confirming the successful grafting of In(III) onto the ATP particles. The XRD pattern of ATP shows typical peaks for pure ATP that appeared at $2\theta = 20.0^\circ$ and 35.2° (Fig. 5). The peaks of SIA are narrower and less intense than pure ATP, with new peaks present. However, a peak assignable to crystalline In_2O_3 could not be clearly seen in the SIA spectrum. This might be because In_2O_3 nanoparticles were highly dispersed on the surface of the ATP carrier and the diffraction peak intensity of In_2O_3 was very weak because of interference from ATP.

Fig. 1. SEM images of ATP (a), SA (b), n-SIA (c), and SIA (d) samples.

Fig. 2. TEM images of ATP (a), SA (b), n-SIA (c), and SIA (d) samples.

Fig. 4. XPS spectra of SA (1) and SIA (2) with expansions of S 2p (3) and In 3d (4).

Fig. 5. XRD patterns of ATP (1) and SIA (2).

3.2. Performance of catalysts for converting glucose into HMF

The conversion of glucose to HMF by the catalysts was trialed with various solvent systems (Table 1). Using water as the solvent afforded a relative low HMF yield (Table 1, entry 1). A catalytic activity test was performed for ATP, SA, n-SIA and SIA in a solvent system consisting of GVL and 10 wt% of water to establish the most appropriate catalyst (Table 1, entries 2–5). Unadulterated ATP had little catalytic activity, resulting in a poor yield of HMF (10.5%). The sulfated ATP, SA, showed higher activity for glucose dehydration with a 17.7% HMF yield. The yield of HMF was 18.4% and 40.2% in the presence of n-SIA and SIA, respectively. This is because the introduction of In(III) to the ATP carrier provides more acidic sites than pure ATP. The catalytic activity of SIA is much higher than that of n-SIA, which is attributed to an elevation of the surface area (from 31.2 to 48.3 m²/g) and pore volume (from 0.103 to 0.189 cm³/g).

The production of HMF from glucose in different systems using homogeneous Lewis acid InCl₃ as the catalyst was studied (Table 1, entries 6–8). An aqueous medium afforded a relatively low HMF yield. When a biphasic solvent system was used, glucose dehydration took place in the aqueous layer followed

Table 1

Conversion of glucose to HMF in various catalytic systems.

Entry	Catalyst	Solvent	Conv. (%)	Yield (%)		Sel. (%)
				HMF	LA	
1	SIA	H ₂ O	60.0	10.7	0.5	17.8
2	ATP	GVL:H ₂ O (9:1)	58.9	10.5	9.1	17.8
3	SA	GVL:H ₂ O (9:1)	65.4	17.7	7.0	27.1
4	n-SIA	GVL:H ₂ O (9:1)	75.5	18.4	11.2	24.4
5	SIA	GVL:H ₂ O (9:1)	76.1	40.2	18.2	52.8
6	InCl ₃	H ₂ O	65.0	21.0	15.5	32.3
7	InCl ₃	NaCl-THF:H ₂ O (9:1)	59.0	23.5	7.3	39.8
8	InCl ₃	NaCl-GVL:H ₂ O (9:1)	56.6	31.0	6.7	54.8

Reaction conditions: Glucose 0.6 g (2 wt%), catalyst 60 mg (10 wt%), solvent 30 g, 180 °C, 60 min.

by extraction of HMF to the organic layer. The isolation of the HMF in the organic layer protects HMF from catalyst contact and minimized side reactions [27]. Saturating the aqueous layer with NaCl diminishes the solubility of both HMF and the organic solvent, improving the organic extraction efficiency [28]. Both the organic solvents used, THF and GVL, were completely miscible with water alone and formed a single-phase mixture before reaction. The use of miscible solvents is preferable because it lowers the chance of mixing problems that may be encountered when scaling up a process [23]. A higher yield of HMF was obtained in the heterogeneous SIA/GVL:H₂O system than with a biphasic InCl₃/NaCl-GVL:H₂O system. A potential advantage of the SIA/GVL:H₂O system is that the addition of salt was not necessary, allowing the homogeneous catalyst (InCl₃) to be replaced by a solid acid catalyst (SIA).

3.3. Effect of reaction parameters on the conversion of glucose

The effects of reaction temperature, reaction time and acid concentration on the conversion of glucose to HMF were studied (Fig. 6). The maximum HMF yield of 40.2% was obtained at 180 °C for 1 h. Although the catalytic activity of SIA was enhanced with the increasing temperature, higher temperatures resulted in side reactions and lowered HMF production [29]. Furthermore, reacting for long periods at higher temperature promoted the decomposition of the HMF. HMF yield increased with the amount of catalyst used and reached a maximum value at 10 wt% of SIA. We concluded that SIA could be used as a potential catalyst for the preparation of HMF from glucose.

3.4. Conversion of fructose into HMF in different catalytic systems

Given that SIA rendered the solution acidic and catalyzed glucose conversion, fructose dehydration was investigated to provide insight into the catalytic activity of our system. The catalysts SIA and InCl₃ were compared in a range of solvents for the conversion of fructose to HMF and LA (Fig. 7). The dehydration of fructose to HMF is faster than that of glucose, with near complete conversion in 60 min for all the systems trialed. The maximum HMF yield from fructose was higher (46.2%) than that from glucose (40.2%). After HMF has been formed, it can undergo further reaction to form equimolar amounts of LA

Fig. 6. The influence of reaction temperature (a), reaction time (b) and acid concentration (c) on glucose dehydration. Reaction conditions: Glucose 0.6 g (2 wt%), GVL:H₂O (9:1) 30 g; (a) catalyst 60 mg (10 wt%), 60 min; (b) catalyst 60 mg (10 wt%), 180 $^{\circ}\text{C}$; (c) 180 $^{\circ}\text{C}$, 60 min.

Fig. 7. Conversion of fructose to HMF in various solvents. Reaction conditions: fructose 0.6 g (2 wt%), catalyst 60 mg (10 wt%), GVL:H₂O (9:1) 30 g, 180 $^{\circ}\text{C}$, 60 min.

Fig. 8. Catalyst recycling experiment with SIA. Reaction conditions: glucose 0.6 g (2 wt%), catalyst 60 mg (10 wt%), GVL:H₂O (9:1) 30 g, 180 $^{\circ}\text{C}$, 60 min.

and formic acid. A common degradation product of the dehydration of hexoses is solid humins formed by the cross-polymerization of glucose and HMF. Humins were not detected in our system, which is possibly because GVL solubilizes humins, thereby minimizing deposition of carbon on the solid catalyst surface and facilitating the separation of the product [23].

3.5. Catalyst recycling experiments

We next studied the activity losses of recycled SIA. The catalyst was separated after the dehydration reaction, washed with anhydrous ethanol, and then dried at 80 $^{\circ}\text{C}$ for 12 h before use. HMF yield from glucose decreased notably with subsequent uses of SIA (Fig. 8). On the 4th cycle, the reaction yield recovered to 32.5% of HMF, but was still lower than that of first cycle. The decreased activity might be because of the loss of active groups during the regeneration process [30]. Moreover, soaking the catalyst in H₂SO₄ was beneficial and reclaimed some of the lost activity. An HMF yield of 35.1% was obtained after this treatment during the recycling steps. Further research will focus on the regeneration of the active groups to maintain the catalytic activity of SIA.

4. Conclusions

SO₄²⁻/In₂O₃-ATP was used as an excellent solid acid catalyst for the preparation of HMF from hexose. The Lewis and Brönsted acid sites on SO₄²⁻/In₂O₃-ATP can catalyze glucose isomerization and fructose dehydration. A 40.2% yield of HMF from glucose was obtained at 180 $^{\circ}\text{C}$ for 60 min in a miscible GVL:H₂O system. The use of this system allowed replacement of a homogeneous catalyst with a solid acid catalyst for glucose isomerization.

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Graphical Abstract

Chin. J. Catal., 2016, 37: 1362–1368 doi: 10.1016/S1872-2067(15)61096-8

Efficient production of 5-hydroxymethylfurfural from hexoses using solid acid $\text{SO}_4^{2-}/\text{In}_2\text{O}_3$ -ATP in a biphasic system

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Efficient and selective production of platform chemical 5-hydroxymethylfurfural (HMF) from hexoses was achieved in the presence of a natural attapulgite-based catalyst, $\text{SO}_4^{2-}/\text{In}_2\text{O}_3$ -ATP. Under optimal conditions, HMF yields from glucose and fructose were 40.2% and 46.2%, respectively.

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双相体系中凹凸土负载型固体酸 $\text{SO}_4^{2-}/\text{In}_2\text{O}_3$ -ATP 催化己糖降解5-羟甲基糠醛申 越^a, 康玉茹^b, 孙建奎^a, 王 超^a, 王 波^{a,*}, 许 凤^a, 孙润仓^{a,#}^a北京林业大学材料科学与技术学院林木生物质化学北京市重点实验室, 北京 100083^b中国科学院兰州化学物理研究所盱眙凹土应用技术研究发展中心, 甘肃兰州 730000

摘要: 凹土 (ATP) 有“千用之土、万土之王”之美誉, 我国江苏省盱眙凹土矿资源量占世界储量的 49% 和我国储量的 74%。ATP 是一种天然链层状结构的含水镁铝硅酸盐黏土矿物, 其分子式为 $(\text{Mg}, \text{Al})_4(\text{Si})_8(\text{O}, \text{OH}, \text{H}_2\text{O})_{26} \cdot n\text{H}_2\text{O}$ 。ATP 具有一定酸性, 层结构中的结构羟基可形成 Brønsted 酸位点, 暴露的 Al^{3+} 离子可形成 Lewis 酸位点。ATP 经酸化或离子交换后作为催化剂直接应用较少。由于 ATP 具有较大的比表面积和较好的热稳定性, 是良好的催化剂载体, 因此多将 ATP 作为载体负载催化活性组分制备负载型催化剂。

5-羟甲基糠醛 (HMF) 是由生物质得到的十二种平台化合物之一, 是非常重要的中间体, 可用于生产呋喃类衍生物, 制备精细化学品、液体燃料和多种聚合物, 还可生产 5-羟基-4-酮-2-戊烯酸和乙酰丙酸. γ -戊内酯 (GVL) 是一种乙酰丙酸的加氢产物, 可以代替乙醇作为汽油添加剂, 也可用来生产丁烯同分异构体等化学品.

本文以天然 ATP 为载体, 通过浸渍-焙烧法设计和制备了兼具 Brønsted 酸和 Lewis 酸的新型固体酸催化剂 $\text{SO}_4^{2-}/\text{In}_2\text{O}_3\text{-ATP}$. 该催化剂可催化己糖直接转化为 HMF. ATP 固有的微观结构和高比表面积使反应选择性提高. 同时, 结合固体酸活性位表征技术探索了己糖转化历程和 HMF 生成机制. 结果表明, In(III) 的引入使 ATP 催化性能更加优越. 固体酸的 Lewis 酸位和 Brønsted 酸位能分别有效催化葡萄糖异构和果糖脱水. 优化的最佳反应条件为: GVL:H₂O 双相体系比例 9:1, 反应温度 180 °C, 反应时间 60 min. 底物为葡萄糖时, HMF 最高收率为 40%. $\text{SO}_4^{2-}/\text{In}_2\text{O}_3\text{-ATP}$ 固体酸比纯 ATP 酸性更强, 可重复使用 4 次, 且不腐蚀设备, 后处理简单, 绿色环保.

关键词: 固体酸催化剂; 凹土; 5-羟甲基糠醛; 双相体系; 果糖脱水; 葡萄糖异构化

收稿日期: 2016-02-19. 接受日期: 2016-03-25. 出版日期: 2016-08-05.

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基金来源: 中央高校基本科研业务费专项资金 (TD2011-11, BLYJ201519); 北京高等学校青年英才计划 (YETP0765); 国家自然科学基金 (31170556); 新世纪优秀人才支持计划 (NCET-13-0671); 国家林业局 (201204803).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).