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Facile preparation of Sn- β zeolites by post-synthesis (isomorphous substitution) method for isomerization of glucose to fructose

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ABSTRACT

Sn- β zeolites were facilely synthesized by a post-synthesis method consisting of two steps, i.e., heteroatom removal and isomorphous substitution by reaction with SnCl₄. This significantly shortened the Sn- β zeolite preparation time from the previously reported 40 d to less than 1 d. It was shown that Sn- β samples prepared using the post-synthesis method had higher Sn contents than that prepared using a hydrothermal method. The as-synthesized Sn- β zeolites were tested in the isomerization of glucose to fructose in aqueous media. The effects of reaction temperature, reaction time, catalyst amount, solvent, and halide additive on the isomerization reaction over Sn-Al- β zeolites were studied in detail. Under the optimized conditions, the yield of fructose reached a maximum of ~43%. The catalysts can be reused without loss of activity after regeneration by calcination.

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1. Introduction

The use of alternative energy sources is attracting increasing attention, because of the current high consumption of fossil resources and concomitant serious environmental problems [1]. Biomass is considered a promising feedstock for the production of biobased chemicals due to its renewable and carbon-neutral properties [1]. Some progress in the catalytic conversion of saccharides to valuable chemicals such as 5-hydroxymethylfurfural (HMF) has been achieved [2–4]. HMF, which is a versatile chemical intermediate, can be easily obtained by dehydration of fructose in acid-catalyzed systems [5–7]. However, the natural abundance of fructose is low, so the

production cost of fructose-based HMF is high. Glucose is the most abundant and widespread monosaccharide, and could be a good candidate as a source of HMF [8]. However, the efficient conversion of glucose to HMF remained a challenge until Zhao et al. [6] reported that CrCl₃ could catalytically convert glucose to HMF in an ionic liquid. The direct conversion of glucose to HMF consists of two steps: the isomerization of glucose to fructose and the dehydration of fructose to HMF [9,10]. The critical issue is how to achieve effective glucose isomerization to fructose in suitable reaction media.

Typical approaches for isomerizing glucose include base-catalyzed and enzymatic techniques. For base-catalyzed isomerization, excess homogeneous inorganic bases in aqueous

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solution are generally used, but fructose has very poor stability in strongly basic systems [11,12]. Although enzymatic isomerization can effectively produce fructose, it is sensitive to operating conditions, such as pH, temperature, and feedstock purity, and requires a long treatment time.

Sn- β zeolites, which are Lewis acids and potential heterogeneous catalysts, are used in a number of reactions such as Baeyer-Villiger oxidation of cyclic ketones [13], the cyclization of citronellal to isopulegol (cyclic carbonylene reaction) [14], and Meerwein-Ponndorf-Verley-Oppenauer redox reactions [15]. Recently, Moliner et al. [16] effectively isomerized glucose to fructose over Sn- β zeolites in aqueous media, and Sn- β zeolites have also been used in the isomerization of xylose and the one-pot synthesis of HMF or 5-(ethoxymethyl)furfural from glucose [10,17,18]. However, the preparation of Sn- β zeolites by traditional hydrothermal methods is unacceptably long, generally requiring about 40 d to achieve full crystallization. Chang et al. [17] recently reported a rapid synthesis of Sn- β zeolites using a modified seeding method, but it still required about 2 d. More importantly, all of the above synthesis procedures cause environmental pollution, e.g., by fluorides [13,17–19]. It is therefore desirable to find eco-friendly and rapid ways of preparing Sn- β zeolites. Post-synthesis (isomorphous substitution) through a solid-gas reaction of highly siliceous zeolites with metal chloride vapors can implant quantities of metal atoms into the zeolite framework. Because the siliceous zeolite precursors have already been crystallized, post-synthesis avoids the need for crystallization of the Sn- β zeolites, as reported in the literature [10,13,16–18], substantially reducing the synthesis time. Isomorphous substitution methods for preparing Sn- β zeolites may have advantages in terms of commercialization and environmental protection.

In this paper, we report the facile preparation of Sn- β zeolites through isomorphous substitution of dealuminated/deboronated zeolites with SnCl₄ vapor, and use of these zeolites to catalyze isomerization of glucose to fructose in aqueous media.

2. Experimental

2.1. Materials

Anhydrous SnCl₄ (AR) was purchased from Sinopharm (China), glucose monohydrate (AR) was purchased from Tianjin Kermel (China), and HNO₃ (65%, AR) was purchased from Beijing Chemical Plant. Al- β zeolite was obtained from the Shenyang University of Chemical Technology (China). B- β zeolite was obtained from Dalian University of Technology. Deionized water was supplied by Dalian University of Technology. All chemicals were used as received, without further purification.

2.2. Catalyst synthesis

The Sn-Al- β catalysts (prepared using Al- β zeolite as the precursor) were prepared using a previously reported post-synthesis method [13]. The preparation involved dealumination and isomorphous substitution with SnCl₄ vapor. The Al- β zeolite (H-form, Si/Al atomic ratio 15) was treated in 4 mol/L

HNO₃ at 348 K for 2 h, with a solid/liquid ratio of 1 g/10 mL, followed by drying at 393 K for 2 h and calcination in air at 813 K for 5 h, resulting in a highly siliceous zeolite (Si/Al atomic ratio 221:1). In the isomorphous substitution, the dealuminated β zeolite was pretreated in a quartz tubular reactor at 813 K for 2 h under a N₂ flow. Then the N₂ flow was diverted to an anhydrous SnCl₄ liquid in a glass bubbler and the SnCl₄ vapor was carried by the N₂ flow to contact the sample bed for a defined time. After the treatment, the sample was purged with pure N₂ at 813 K for 2 h to remove any residual SnCl₄ from the sample powder. After cooling to room temperature under N₂, the treated sample was washed three times with ethanol and then dried in air at 373 K overnight. Finally, the sample was calcined at 813 K for 4 h.

Sn-B- β catalysts (synthesized using B- β zeolite as the precursor) were prepared using a post-synthesis method reported in the literature [20]. B- β zeolite (Si/B atomic ratio 11) was treated in 1 mol/L HCl at 333 K for 2 h, with a solid/liquid ratio of 1 g/10 mL, resulting in a highly siliceous zeolite (Si/B atomic ratio 793:1). The isomorphous substitution process was the same as that for the Al- β zeolite.

For comparison experiments, an Sn- β zeolite was synthesized by hydrothermal methods [21,22]. Tetraethyl orthosilicate (TEOS) was hydrolyzed in an aqueous solution of tetraethylammonium hydroxide (TEAOH) under stirring. Then an aqueous solution of SnCl₄·5H₂O was added, and the mixture was stirred until the ethanol formed by hydrolysis of TEOS was evaporated. HF was added to the clear solution obtained, and a thick paste was formed. Finally, an aqueous suspension of dealuminated nanocrystalline (20 nm) β zeolite “seed” was added. The final gel composition was 1.0 SiO₂:0.008 SnO₂:0.54 TEAOH:7.5 H₂O:0.54 HF. The crystallization was carried out in a Teflon-lined stainless-steel autoclave, which was heated to 413 K and rotated for a period of 20 d.

2.3. Characterization methods

The structures of the β zeolite samples were determined by X-ray diffraction (XRD; Rigaku D/Max 2400), using Cu K α radiation at a scanning rate of 8°/min between 5° and 50°. The amount of Sn was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES; Perkin OPTIMA-2000DV). Ultraviolet-visible (UV-Vis) spectra were obtained using a Shimadzu UV-550 spectrophotometer, with BaSO₄ as a reference. Fourier-transform infrared (FT-IR) spectra were recorded with a Bruker EQUINOX55 spectrometer, from 4000 to 400 cm⁻¹, using KBr pellets.

2.4. Catalytic tests

Glucose isomerization was carried out in 1 mL thick-walled glass reactors heated in a Reacti-Therm I Heating/Stirring Module (Thermo Scientific). In a typical run, 0.4 mL of an aqueous solution consisting of 10 wt% glucose and 30 mg of catalyst were placed in the reactor. The reactor was sealed and put in the module at a defined temperature, under stirring, for a defined reaction time, ranging from 15 min to 2 h. The reaction

was quenched by rapid cooling in an ice bath. The reaction solution was diluted and filtered, and then a small amount of clear filtrate was removed for analysis. The samples were analyzed by high-performance liquid chromatography, using an Agilent 1200 system. Glucose and fructose were monitored using a refractive index detector with a Biorad Aminex HPX-87H column. The mobile phase was freshly prepared 0.005 mol/L H_2SO_4 ; the analysis conditions were flow rate 0.5 mL/min, column temperature 338 K, detector temperature 323 K. A small amount of mannose was produced during the isomerization. However, the response factors of fructose and mannose are nearly identical; therefore, the column did not separate them well, so they were treated as a single compound and quantified based on the response factor of fructose.²³ The amounts were calculated by an internal standard method with 1,2-propanediol as the standard.

3. Results and discussion

3.1. Catalyst characterization

As can be seen in Fig. 1, all samples (Al/B β , dealuminated/deboronated β , and isomorphously substituted Sn-Al/B β zeolites) had obvious diffraction peaks at $2\theta = 7.80^\circ$, 13.45° , 21.38° , 22.43° , 25.34° , 27.09° , and 29.60° . These results demonstrated that the samples had well-defined BEA topologies [24]. The Sn-B- β and Sn-Al- β zeolites also had a diffraction line at $2\theta = 26.7^\circ$, which is characteristic of bulk SnO_2 . The patterns had similar diffraction intensities, indicating that no significant collapse of the crystalline structure occurred after dealumination or deboronation and SnCl_4 vapor treatment.

The Sn contents of Sn- β zeolites synthesized via different methods were determined using ICP-AES (Table 1). As can be seen, the Sn- β samples prepared using post-synthesis had much higher Sn contents than that prepared hydrothermally. In addition, B was easily removed from the framework by acid treatment, leading to an increase in the Si/B atomic ratio from 11 to 793. The Sn content of the Sn-B- β sample was 5.95%. However, Al was relatively difficult to remove from the framework. The Si/Al atomic ratio increased from 15 to 222. The Sn content in the Sn-Al- β sample was about 3.30%. In general, the

Table 1

Sn contents of Sn- β zeolites synthesized by different methods.

Sample	Si/Al or Si/B	SnO_2 content (wt%)
Sn- β	—	1.95
Sn-Al- β	222	3.30
Sn-B- β	793	5.95

post-synthesis method improved the Sn loading on the β zeolites, and circumvented the use of hazardous HF.

UV-Vis spectroscopy was used to verify the coordination states of Sn in the samples (Fig. 2). As illustrated, the three Sn- β samples all had clear absorption bands at ~ 220 nm, assigned to tetrahedrally coordinated Sn in the zeolite framework [25]. Shoulder bands at ~ 255 – 300 nm were also observed, implying the presence of extra-framework Sn species [13]. The 255–300 nm peak intensities of the post-synthesized samples were stronger than that of the hydrothermal sample, suggesting that more extra-framework Sn species formed during the post-synthesis procedure. The absorption band at ~ 260 nm was assigned to small extra-framework SnO_2 species [26]. The post-synthesized samples had an absorption band centered at ~ 290 nm, which indicated the formation of bulk SnO_2 (assigned to hexacoordinated polymeric Sn species [27]), consistent with the XRD results. The UV-Vis band of Sn- β centered at ~ 260 nm reflects a smaller SnO_2 domain [28]. All three samples contained both framework Sn and extra-framework Sn species. Unlike the hydrothermal sample, the post-synthesized samples contained bulk SnO_2 species as well as framework Sn and small extra-framework SnO_2 species.

The FT-IR spectra of the β zeolites before and after deboronation or dealumination, and those after post-synthesis with SnCl_4 vapor, are shown in Fig. 3. The Al- β and B- β zeolites showed obvious Si–O–Al and Si–O–B absorption bands at 960 and 956 cm^{-1} . After treatment with acid, strong absorption bands appeared at around 960 cm^{-1} , which indicates the formation of Si–OH defect groups [29]. However, for the Sn- β zeolites prepared by post-synthesis with SnCl_4 vapor, the bands at around 960 cm^{-1} are believed to be attributable to the stretching vibrations of Si–O tetrahedra bonded to Sn atoms, forming Si–O–Sn bonds [30]. Furthermore, the strongest absorption

Fig. 1. XRD patterns of β zeolite samples.

Fig. 2. UV-Vis spectra of Sn- β samples.

Fig. 3. FT-IR spectra of β zeolites.

bands, at about 1085 and 1095 cm^{-1} , for the Al- β and B- β zeolites, respectively, shifted to higher wave numbers after acid treatment, which also indicates that Al or B had been removed from the zeolite framework [31].

3.2. Isomerization of glucose to fructose

3.2.1. Effects of reaction temperature and reaction time

Sn- β zeolites have been shown to be effective heterogeneous catalysts for the isomerization of glucose to fructose in aqueous solutions, and could therefore be used in biorefining of carbohydrates [16]. We therefore investigated the isomeriza-

tion of glucose in the presence of the as-synthesized Sn- β zeolites. Figure 4 shows the effects of reaction temperature and time on the isomerization reaction over the synthesized Sn-Al- β sample. When the glucose isomerization was carried out at 353 K for 2 h, the fructose yield was only 10%; at 393 K, the fructose yield increased to ~40% after only 1 h. The isomerization of glucose to fructose is slightly endothermic [16], so increasing the reaction temperature should improve the glucose conversion and fructose yield. When the temperature was further increased to 403 K, the glucose conversion increased, but the fructose yield reached a maximum value after 0.5 h. When the reaction time was extended, the fructose yield decreased a little; unknown products such as dehydration by-products and humins from fructose, produced at higher temperatures after longer times, may account for the decreased amount of fructose [32]. The optimum reaction conditions for glucose conversion and fructose yield were at 393 K for 2 h.

3.2.2. Effects of catalyst dosage

The effects of catalyst dosage on the isomerization of glucose over the Sn-Al- β zeolite were investigated; the results are shown in Fig. 5. A blank test (393 K, 2 h) showed that the isomerization of glucose to fructose could not proceed without a catalyst in an aqueous medium. When 10 mg of catalyst was added to the glucose solution, the glucose conversion and fructose yield were ~40% and ~30%, respectively. When the catalyst dosage was increased to 20 mg, the glucose conversion and fructose yield increased to more than 50% and 40%, respectively. Further increases in the catalyst dosage had a negligible effect on the fructose yield, but the glucose conversion was significantly improved, possibly because the amount of Sn-Al- β catalyst (20 mg) was already sufficient for glucose isomerization under the specified conditions, and the Lewis acidity of the excess catalyst caused more side reactions.

The XRD and UV-Vis results suggest that more extra-framework small SnO_2 species and bulk SnO_2 are present in the post-synthesized samples than in the hydrothermal sample. When the reaction conditions were water as the solvent, glucose concentration 10 wt%, reaction temperature 393 K, and time 2 h, the glucose conversions over the hydrothermal Sn- β , Sn-Al- β , and Sn-B- β zeolites were ~66%, ~66%, and ~65%,

Fig. 4. Effects of reaction temperature and reaction time on isomerization of glucose to fructose over Sn-Al- β catalyst. (a) 353 K; (b) 373 K; (c) 393 K; (d) 403 K. (1) Glucose conversion; (2) Fructose yield. Reaction conditions: 10 wt% glucose aqueous solution 0.4 mL, Sn-Al- β 30 mg.

Fig. 5. Effect of Sn-Al- β catalyst dosage on isomerization of glucose to fructose. Reaction conditions: 10 wt% glucose aqueous solution 40 mL, 393 K, 2 h.

respectively, and the fructose yields were ~46%, ~43%, and ~43%, respectively. This indicated that the extra-framework SnO_2 and bulk SnO_2 did not negatively affect glucose isomerization. It is generally accepted that only framework Sn species provide active sites for reactions with Sn- β zeolite catalysts [21,23], so it is concluded that all three Sn-containing samples had similar amounts of framework Sn species.

3.2.3. Effects of solvent

The effects of the solvent on the isomerization of glucose to fructose were investigated, and the results are shown in Fig. 6. Three ionic liquids with different anions, namely 1-butyl-3-methylimidazolium chloride ([bmim]Cl), 1-ethyl-3-methylimidazolium bromide ([emim]Br), and 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF₆), and three strongly polar organic solvents, namely *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMA), and dimethyl sulfoxide (DMSO), were used. Glucose was completely soluble in all these solvents. When the ionic liquids were used as the solvents, no fructose was produced, although significant glucose conversions were observed. In terms of possible glucose isomerization mechanisms [33], ionic liquids could inhibit contact and reaction between the Sn- β zeolite and glucose molecules. As

Fig. 6. Isomerization of glucose to fructose in different solvents. (1) [bmim]Cl; (2) [emim]Br; (3) [bmim]PF₆; (4) DMSO; (5) DMF; (6) DMA; (7) Water. Reaction conditions: glucose monohydrate 50 mg, solvent 0.4 mL, Sn-Al- β catalyst 30 mg, 393 K, 2 h.

Fig. 7. Effects of solvent composition on isomerization of glucose to fructose. (1) 0.4 mL A; (2) 0.3 mL A + 0.1 mL B; (3) 0.2 mL A + 0.2 mL B; (4) 0.1 mL A + 0.3 mL B; (5) 0.4 mL B. A water; B [bmim]Cl. Reaction conditions: glucose monohydrate 50 mg, Sn-Al- β catalyst 30 mg, 393 K, 2 h.

shown in Fig. 7, the fructose yield decreased continuously with increasing proportion of ionic liquid in the mixed solvent. However, when organic solvents were used in the reaction system, the fructose yields were 4.9%, 16.2%, and 29.7% in DMSO, DMF, and DMA, respectively, possibly because the organic solvents, which are Lewis bases, competed with glucose for the Lewis acid sites in the Sn-Al- β zeolite. Strong interactions between Lewis acid centers in zeolites and hydroxyl/carbonyl moieties in reactants dissolved in organic solvents have been reported previously [34].

3.2.4. Effects of sodium halide additives

Ionic liquids such as [bmim]Cl essentially suppressed glucose isomerization, so it was speculated that the anion could be an influential factor. Experiments were performed to examine the effects of anions. Various sodium halides, i.e., NaF, NaCl, NaBr, and NaI, were used as additives under the same reaction conditions. The glucose conversions and fructose yields are listed in Table 2. The results indicated that under these reaction conditions, no cross reactions occurred. NaI had a negligible

Table 2

Effects of sodium halide additives on isomerization of glucose to fructose.

Dosage (mg)	Salt	Glucose conversion (%)	Fructose yield (%)
—	—	66.1	43.0
10	NaF	40.3	20.1
10	NaCl	62.1	33.6
10	NaBr	63.1	33.1
10	NaI	65.1	38.0
30	NaF	37.4	22.8
30	NaCl	56.4	28.9
30	NaBr	52.4	27.0
30	NaI	64.8	37.1
50	NaF	35.2	22.6
50	NaCl	52.4	25.7
50	NaBr	49.2	24.6
50	NaI	61.6	35.7

Reaction conditions: 10 wt% glucose aqueous solution 0.4 mL, Sn-Al- β 30 mg, 393 K, 2 h.

Table 3Reusability of Sn-Al- β catalyst in glucose isomerization.

Sample	Glucose conversion (%)	Fructose yield (%)
Fresh catalyst	54.7	43.2
Regeneration I	57.2	45.6
Regeneration II	56.9	46.5
Regeneration III	59.9	45.8

Reaction conditions: 10 wt% glucose aqueous solution 8.0 mL, Sn-Al- β 600 mg, 393 K, 2 h.

effect on the reaction, but NaCl and NaBr inhibited the isomerization reaction to a certain degree. When the dosages of NaCl and NaBr were increased from 10 mg to 50 mg, the fructose yields decreased from ~33% to about ~25%. This indicated that chloride and bromide anions probably interacted with the active sites, i.e., Sn centers, thereby suppressing glucose isomerization and leading to decreased fructose yields. NaF significantly lowered the fructose yield. When only 10 mg of NaF were added to the mixture, the fructose yield dropped from ~43% to ~20%. It was previously reported that sodium halides increased the salting-out effect on glucose in aqueous solutions [35,36]. The order of the salting coefficients (k_s) are as follows: NaF > NaCl > NaBr. NaF had the strongest salting-out effect on glucose. These results show that the fructose yields were related to the salting-out effects of sodium halides. The isomerization of glucose to fructose over the Sn-Al- β catalyst was high in water without sodium halides, which could be the reason for [bmim]Cl had a negative effect on the isomerization, as shown in Fig. 6.

3.2.5. Catalyst reusability

The Sn-Al- β zeolite was used to study the reusabilities of the synthesized zeolites in the isomerization of glucose. It was found that carbonaceous deposits formed during the reaction, resulting in a decrease in the fructose yield from 43.2% in the first run to 39.8% in the second run (without regeneration; the catalyst was filtered and dried at 393 K before reuse). To eliminate the effects of carbonaceous deposits, the Sn-Al- β catalyst was regenerated by calcination at 813 K for 4 h after each run, and reused four times. The results are listed in Table 3. (When the reaction was scaled up by a factor of 20, the glucose conversion was a little lower than those in Fig. 1, possibly because of reduced stirring efficiency.) These results show that there are no substantial changes in the glucose conversion and fructose yield over the regenerated catalyst compared with those over the fresh catalyst, indicating that the as-synthesized Sn- β catalysts can effectively be separated and reused.

4. Conclusions

In this work, a facile preparation of Sn- β zeolites by post-synthesis is presented. The post-synthesis method consisted of two procedures, i.e., heteroatom removal and isomorphous substitution by reaction with SnCl₄; the preparation time was reduced from about 40 d (reported for zeolites prepared hydrothermally) to less than 1 d, and the use of hazardous HF was avoided. The Sn contents of the Sn- β zeolites syn-

thesized using the post-synthesis procedure were higher than that of the zeolite prepared using a hydrothermal method, and both framework and extra-framework Sn species were present. The activities of the as-synthesized Sn- β zeolites in the isomerization of glucose to fructose in aqueous solutions were comparable to that of the zeolite synthesized hydrothermally. The maximum fructose yield of ~43% was obtained at a glucose conversion of ~66% at 393 K for 2 h. It was found that the reaction solvent played a key role in the isomerization of glucose; water was the best solvent. Ionic liquids suppressed the Sn- β -zeolite-catalyzed isomerization of glucose. Low or moderate yields of fructose were achieved in organic solvents such as DMSO, DMF, and DMA, possibly because the organic solvents, which are Lewis bases, competed with glucose for the Lewis acid sites in the Sn-Al- β zeolite. The as-synthesized Sn- β zeolites could be reused three times in the isomerization of glucose to fructose without loss of activity, after regeneration procedures. These facilely prepared Sn- β zeolites have potential applications in biomass conversion.

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Graphical Abstract

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Facile preparation of Sn- β zeolites by post-synthesis (isomorphous substitution) method for isomerization of glucose to fructose

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Sn- β zeolites were facilely synthesized using a post-synthesis method, which significantly shortened the preparation time. The effects of the reaction conditions on glucose isomerization over the Sn- β zeolites were studied in detail.

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二次法(同晶取代)快速合成Sn- β 沸石用于葡萄糖异构制果糖

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摘要: 采用二次法快速合成了Sn- β 沸石. 该方法包含杂原子脱除和与SnCl₄的同晶取代两个步骤, 合成时间从水热法的约40 d缩短为少于1 d, 且Sn含量更高. 将该沸石用于水相催化葡萄糖异构化制果糖反应, 详细考察了反应温度、时间、催化剂用量、溶剂以及卤盐添加物对反应性能的影响. 在优化的反应条件下, 果糖收率最高可达约43%. 催化剂可以通过焙烧再生.

关键词: Sn- β ; 同晶取代; 葡萄糖; 异构化; 果糖

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1. 前言

随着大量化石能源的使用和随之而来的严重环境问题, 人们越来越重视可再生能源的开发利用^[1]. 由于具有可再生和碳平衡的特点, 生物质被认为是生产生物

基化学品的重要原料^[1]. 糖催化转化制备高附加值化学品, 如5-羟甲基糠醛(HMF), 已经取得了进展^[2-4]. HMF是一种多用途化学中间体, 可以经由酸催化果糖水解得到^[5-7]. 然而, 果糖在自然界中的储量低, 增加了HMF的制备成本. 而葡萄糖是自然界储量最大、分布最广泛

的单糖,有望成为制备HMF的绝佳原料^[8]。Zhao等^[6]首次报道了离子液体中 CrCl_3 催化葡萄糖制得HMF。葡萄糖直接转化为HMF实际包含两个步骤:葡萄糖异构为果糖和果糖脱水得到HMF^[9,10],其中第一步是该反应的关键。

典型的葡萄糖异构工艺有碱催化 and 酶催化技术。碱催化需要过量的有机碱水溶液,而果糖在强碱体系中极不稳定^[11,12];虽然酶催化可高效制备果糖,但操作条件过于敏感,如pH值,温度,原料纯度等,而且反应时间一般很长。

$\text{Sn-}\beta$ 是一种含有L酸的多相催化剂,已用于很多反应中:如环酮的Baeyer-Villiger (BV) 氧化反应^[13],香茅醛环化为异薄荷醇^[14],以及Meerwein-Ponndorf-Verley-Oppenauer氧化还原反应^[15]。最近,Moliner等^[16]以 $\text{Sn-}\beta$ 为催化剂成功在水溶液中将葡萄糖异构为果糖。另外, $\text{Sn-}\beta$ 沸石还可用于木糖异构化,葡萄糖一锅法制备HMF或5-乙氧基甲基糠醛^[10,17,18]。采用水热法制备 $\text{Sn-}\beta$ 沸石的晶化时间太长,约40 d;即使采用快速合成法也需要大约2 d^[17]。同时,上述合成过程都使用氟化物^[13,17–19]。因此,迫切需要一种环保而快速的制备 $\text{Sn-}\beta$ 的路线。二次合成法(同晶取代)经由高硅沸石和金属氯化物的气固相反应可以将大量金属原子插入到沸石骨架中,且不需要水热晶化,大大缩短了时间^[10,13,16–18]。因此,从经济和环保角度考虑,二次合成法在 $\text{Sn-}\beta$ 合成中具有很大优势。

本文采用脱铝/脱硼沸石与 SnCl_4 气固相反应快速制备 $\text{Sn-}\beta$ 沸石,并研究了该沸石在水溶液中催化葡萄糖异构制果糖的性能。

2. 实验部分

2.1. 试剂

无水 SnCl_4 (AR) 购自国药集团。一水葡萄糖(AR)购自天津科密欧化学试剂有限公司。硝酸(65%, AR)购自北京化学试剂厂。 $\text{Al-}\beta$ 沸石来自沈阳化工大学。 $\text{B-}\beta$ 由大连理工大学合成。去离子水由大连理工大学提供。所有试剂在使用前均未进行进一步提纯。

2.2. 催化剂制备

采用二次合成法制备 $\text{Sn-Al-}\beta$ (以 $\text{Al-}\beta$ 为前驱体)^[13]。制备过程包括脱铝和 SnCl_4 同晶取代两步。 $\text{Al-}\beta$ (H型, Si/Al 摩尔比15)以4 mol/L硝酸在348 K下脱铝2 h,固液比1 g/10 ml,然后空气中393 K干燥2 h,813 K焙烧5 h,得到高硅沸石(Si/Al 摩尔比221);再置于石英管反应器

中于813 K用 N_2 吹扫2 h。然后切换为夹带 SnCl_4 蒸汽的 N_2 。反应一定时间后,重新切换为纯 N_2 吹扫2 h以除去残余未反应的 SnCl_4 。降温至室温。样品用乙醇洗涤3次,并在空气中于373 K干燥过夜,最后在空气中813 K焙烧4 h。

采用二次法制备 $\text{Sn-B-}\beta$ (以 $\text{B-}\beta$ 为前驱体)^[20]。将 $\text{B-}\beta$ 沸石(Si/B 摩尔比11)用1 mol/L盐酸在333 K下处理2 h,固液比1 g/10 ml,得到高硅沸石(Si/B 摩尔比793)。随后的同晶取代过程与 $\text{Al-}\beta$ 相同。

为了比较,采用水热法制备 $\text{Sn-}\beta$ 沸石^[21,22]。首先将正硅酸乙酯(TEOS)在四乙基氢氧化铵(TEAOH)水溶液中搅拌水解。然后加入 $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ 水溶液,搅拌,直到TEOS水解产生的乙醇挥发完全。加入HF,得到粘稠糊状物。最后,加入晶种,即20 nm粒度脱铝 β 沸石纳米晶悬浊液。最终胶液组成为 $1.0\text{SiO}_2:0.008\text{SnO}_2:0.54\text{TEAOH}:7.5\text{H}_2\text{O}:0.54\text{HF}$ 。在聚四氟乙烯内衬高压釜中于413 K晶化20 d。

2.3. 催化剂表征

β 沸石的X射线衍射(XRD)表征在Rigaku D/Max 2400型X射线衍射仪上进行。 $\text{Cu K}\alpha$ 辐射源,扫描速度 $8^\circ/\text{min}$,扫描范围 $5^\circ\text{--}50^\circ$ 。 Sn 含量用电感耦合等离子体原子发射光谱(ICP-AES)测定,仪器为Perkin OPTIMA-2000DV型原子发射光谱仪。紫外-可见光谱(UV-Vis)在Shimadzu UV-550型光谱仪上测得, BaSO_4 做参比。傅立叶红外光谱(FT-IR)在Bruker EQUINOX55光谱仪上测得,波数 $4000\text{--}400\text{ cm}^{-1}$,采用KBr压片技术。

2.4. 催化剂评价

葡萄糖异构化反应在配备有Reacti-Therm I型加热/搅拌模块的1 ml厚壁玻璃反应器(赛默飞世尔)中进行。典型过程是,0.4 ml葡萄糖水溶液(10 wt%)和30 mg催化剂加入反应器并密封,加热并搅拌15 min~2 h后,将反应器放入冰浴中使反应终止。反应液稀释分离后,取部分滤液进行产物分析。产物分析在安捷伦1200型高效液相色谱上进行,示差检测器,Biorad Aminex HPX-87H色谱柱,流动相0.005 mol/L H_2SO_4 。检测条件:流速0.5 ml/min,柱温338 K,检测器温度323 K。异构化过程中生成微量甘露糖,由于色谱柱不能完全区分甘露糖和果糖,所以,将甘露糖作为果糖处理^[23]。以1,2-丙二醇为内标物计算组分含量。

3. 结果与讨论

3.1. 催化剂的表征

图1为Al- β 、B- β 、脱铝后的 β 、脱硼后的 β 、Sn-B- β 和Sn-Al- β 样品的XRD谱。由图可见,各样品均在 $2\theta = 7.80^\circ, 13.45^\circ, 21.38^\circ, 22.43^\circ, 25.34^\circ, 27.09^\circ, 29.60^\circ$ 处有明显衍射峰,说明均具有BEA拓扑结构^[24]。Sn-B- β 和Sn-Al- β 在 $2\theta = 26.7^\circ$ 处出现表征大颗粒SnO₂的衍射峰。另外,各样品特征衍射峰强度相近,说明脱硼/脱铝以及SnCl₄气固相反应过程没有对沸石骨架结构造成明显破坏。

不同方法合成的Sn- β 沸石的Sn含量见表1。由于B很容易从骨架中酸处理脱除,所以Sn-B- β 中的Si/B摩尔比由11上升到793; Sn含量高达5.95%。而Al从骨架中的脱除相对困难,Sn-Al- β 中的Si/Al摩尔比仅由15升到222, Sn含量约为3.30%。由此可见,与水热法相比,二次法提高了Sn- β 沸石的Sn含量,且避免使用有毒的HF。

图2为三个Sn- β 样品的UV-Vis谱。可以看出,各样品均在220 nm附近出现表征骨架Sn的明显吸收^[25]。位于255–300 nm的肩峰说明样品中同时含有非骨架Sn^[13],其中二次合成法样品的峰强度强于水热法样品,说明二次合成过程中生成了更多的非骨架Sn。260 nm附近的吸收归属于小颗粒的非骨架SnO₂物种^[26]。二次合成样品中290 nm处的吸收归属于大颗粒SnO₂ (六配位聚合Sn物种^[27]),与XRD结果一致。较低的吸收中心位置(~260 nm)说明水热法Sn- β 中主要是小颗粒的SnO₂^[28]。可见,与水热法样品不同的是,二次法样品除了含有骨架Sn和小颗粒的非骨架SnO₂,还含有大颗粒的非骨架SnO₂。

脱铝/脱硼前后以及同晶取代以后的B沸石的FT-IR谱见图3。可以看出,Al- β 和B- β 均有明显的表征Si–O–Al键和Si–O–B键的吸收(960和956 cm⁻¹)。酸处理后于960 cm⁻¹处的吸收说明有Si–OH空位生成^[29]。而二次合成的Sn-B沸石中960 cm⁻¹波数的吸收归属于与Sn相连组成四配位Si–O–Sn键的Si–O键伸缩振动^[30]。另外,Al-B和B-B中分别位于1085和1095 cm⁻¹处的吸收在酸处理后向高波数移动,也说明Al和B从骨架中脱除^[31]。

3.2. 葡萄糖异构化制果糖

3.2.1. 反应温度和时间的影响

Sn- β 沸石已经被证明是葡萄糖异构为果糖的一种有效的多相催化剂,这为碳水化合物生物精制提供了机会^[16]。基于此,我们考察了所制备的Sn- β 沸石在葡萄糖异构为果糖反应中的性能。图4是反应温度和时间对Sn-Al- β 沸石上葡萄糖异构化反应的影响。反应在353 K进行2 h,果糖收率只有10%;将反应温度升高到393 K,反应1 h后果糖收率达到约40%。葡萄糖异构为果糖是

轻微吸热反应^[16],所以升高温度有利于葡萄糖转化率和果糖收率的提高。当温度提高到403 K,反应0.5 h后果糖收率即达到最大值。继续延长反应时间,果糖收率稍有下降,可能是高温下果糖转化为其他水解副产物和腐殖质等^[32]。为得到较高的葡萄糖转化率和果糖收率,于393 K反应2 h比较合适。

3.2.2. 催化剂用量的影响

图5是催化剂用量对Sn-Al- β 沸石上葡萄糖异构化的影响。空白试验(393 K, 2 h)表明,在没有催化剂的情况下葡萄糖在水相中不会异构化为果糖。当催化剂用量为10 mg时,葡萄糖转化率和果糖收率分别为约40%和30%;至20 mg时两者分别升至50%和40%。继续提高催化剂用量,尽管葡萄糖转化率上升,但果糖收率降低。这可能是由于过量的催化剂提供的过量L酸中心,导致了更多的副反应。

由图1和图2可知,二次合成样品较水热合成样品中含有更多的非骨架小颗粒和大颗粒SnO₂。在水为溶剂,于393 K反应2 h时,Sn- β 、Sn-Al- β 和Sn-B- β 上的葡萄糖转化率分别为~66%、~66%和~65%,对应的果糖产率分别为~46%、~43%和~43%。这表明非骨架Sn物种对葡萄糖异构没有不利影响。一般认为,只有骨架Sn能够提供催化葡萄糖异构的活性中心^[21,23],所以推测含Sn样品中的骨架Sn含量大致相当。

3.2.3. 溶剂的影响

三种含有不同阴离子的离子液体1-叔丁基-3-甲基咪唑氯([bmim]Cl), 1-乙基-3-甲基咪唑溴([emim]Br), 和1-叔丁基-3-甲基咪唑六氟磷酸([bmim]PF₆)和三种强极性有机溶剂N,N-二甲基甲酰胺(DMF), N,N-二甲基乙酰胺(DMA)和二甲基亚砜(DMSO)用于比较溶剂对葡萄糖异构反应性能的影响,结果见图6。葡萄糖在以上溶剂中均可完全溶解。以离子液体为溶剂时,虽然有大量葡萄糖转化,但没有果糖生成。鉴于可能的葡萄糖异构化机理^[33],离子液体可能阻碍了葡萄糖分子与Sn- β 的接触进而反应。如图7所示,果糖收率随着溶剂中离子液体含量的增加而持续降低。而在有机溶剂DMSO, DMF和DMA中果糖的收率分别为4.9%, 16.2%和29.7%,可能是因为这些有机溶剂作为L碱在Sn-Al- β 的L酸中心上发生与葡萄糖分子的竞争吸附。文献也有报道,有机溶剂中沸石L酸中心会与反应物的羟基/羰基发生强相互作用^[34]。

3.2.4. 卤盐添加物的影响

离子液体,比如[BMIM]Cl,极大抑制葡萄糖异构

的原因有可能在于其中的阴离子. 我们在相同的反应条件下考察了一系列卤化钠对反应性能的影响, 结果如表2. 可以看出, 卤化钠的添加不利于葡萄糖异构的进行. 其中NaI的加入对反应的影响较小; 当NaCl和NaBr用量从10 mg增加到50 mg, 果糖收率从约33%降低到约25%. 这说明 Cl^- 和 Br^- 可能与Sn活性中心结合, 阻止了葡萄糖异构化, 进而导致了果糖收率降低. 而仅仅10 mg NaF的加入, 就使得果糖收率从约43%降低到约20%. 有报道指出, 卤化钠会增强水溶液中葡萄糖的盐析效应^[35,36], 其盐效应常数的大小顺序为: $\text{NaF} > \text{NaCl} > \text{NaBr}$. 可见, 果糖收率降低值的变化趋势与卤化钠的盐析效应强度一致. 因此, 在没有卤化钠添加的情况下, Sn-Al- β 在水中表现出很高的葡萄糖异构化能力, 这可能解释了在离子液体[BMIM]Cl中葡萄糖异构化性能降低的原因.

3.2.5. 催化剂重复使用性

以Sn-Al- β 为催化剂, 考察了其在葡萄糖异构化反应中的重复使用性能. 发现反应过程中有积炭产生, 导致果糖收率从第一次使用的43.2%降低到第二次的39.8% (催化剂不再生, 只过滤分离并在393 K干燥后重

复使用). 为避免积炭的影响, 催化剂每次使用然后在813 K焙烧4 h进行再生, 然后用于反应, 重复4次, 结果见表3 (反应放大20倍后, 可能是因为搅拌效率的问题, 葡萄糖转化率和果糖收率均稍有降低). 可以看出, 再生催化剂性能和新鲜催化剂的差别不大, 说明二次合成的Sn-B沸石可以有效从反应体系分离和重复使用.

4. 结论

快捷合成Sn- β 的二次合成法包含杂原子脱除和与 SnCl_4 同晶取代反应两步, 它可将合成时间从水热法的约40 d降至1 d以下, 且无需使用有毒的HF. 与水热法相比, 二次合成法Sn- β 沸石具有更高的Sn含量(包含骨架Sn和非骨架Sn), 且催化葡萄糖异构性能相当, 在水溶液中于393 K反应2 h, 葡萄糖转化率和果糖最大收率分别达到约66%和43%. 溶剂对反应性能的影响很大: 其中水是最好的溶剂; 离子液体阻碍Sn- β 上葡萄糖异构化反应; 在DMSO, DMF和DMA中, 果糖收率较低, 可能是因为这些有机溶剂作为一种L碱, 与催化剂的L酸活性中心上发生竞争吸附. 另外, 催化剂具有很好的重复使用性能, 有望应用于生物质转化领域中.