Chinese Journal of Catalysis 38 (2017) 426–433

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Article (Special Column on Novel Catalysts for Energy and Environmental Issues)

Preparation of Sn-β-zeolite via immobilization of Sn/choline chloride complex for glucose-fructose isomerization reaction

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ARTICLE INFO

Article history:
Received 31 September 2016
Accepted 23 November 2016
Published 5 March 2017

Keywords:
Sn-β zeolite
Immobilization
Choline chloride
Glucose
Isomerization
Fructose

ABSTRACT

Well dispersion of tin species in an isolated form is a quite challenge since tin salts are easily hydrolyzed into (hydr)oxides during aqueous stannation of β-zeolite. In this study, immobilization of tin species on high silica commercial β-zeolite by using $SnCl_2$/Choline chloride (ChCl) complex followed with calcination provided a convenient way to get well dispersed Sn in β-zeolite in the aqueous condition, which was observed based on electron microscopy images, UV visible spectra and X-ray diffraction pattern. The existence of ChCl facilitated tin species to incorporate into zeolite. (1–2) wt% of Sn loaded β-zeolites exhibited good catalytic activity and high selectivity for glucose-fructose isomerization reaction.

1. Introduction

The preparation of Sn-β-zeolite via post-synthetic approaches has been attracted much interest since it is simpler, faster and scalable way compared with the hydrothermal route. The general method to add tin as the Lewis acid site in β-zeolite is based on a two-step way consisted of dealumination of high alumina commercial β-zeolite to generate silanol nest, followed with stannation [1–5]. For instances, Sn-β-zeolite can be obtained via gas-solid deposition of $SnCl_4$ at 400–500 °C [1]. Also, a solid state ion exchange method can result up to 10 wt% of tin incorporated into the framework of zeolite [2,3]. It is reported that (5–6) wt% tin loaded β-zeolites always have high activity [1–3] but the highest turnover frequency (TOF) could be achieved with only small amount of grafted tin (*i.e.* (0.5–2) wt%) [4,5]. For high tin loaded materials (*i.e.* >5 wt%), inactive species (*e.g.* extraframework [1], oligomeric Sn_xO_y [3], oxide form SnO_2) and/or other physical barriers (*i.e.* loss of micropore access) [3,5] are usually observed which make it inefficient in term of tin sustainability. Particularly, such problems could occur in liquid-stannation processes, especially in the presence of water [5,7] or hydroxide ion [6] since tin is easily hydrolyzed and as a result, precipitate is easily formed at this state [7]. Therefore, to obtain Sn-β-zeolite catalyst with good performance, it is important to well disperse tin on the supports and avoid the formation of unwanted tin species during the treatments in aqueous solutions [4,8].

Recently, it is found that the addition of ChCl, a safe and

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This work was supported by Aomori City Government, and the Doctoral Program of Ministry of Education, Culture, Sport, Science, and Technology (MEXT), Japan.

The authors thank Professor Seiichiro Ioka at NJRISE, Hirosaki University helped ICP measurements.

DOI: 10.1016/S1872-2067(17)62754-2 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 3, March 2017

cheap quaternary ammonium chloride [10], can improve tin solubility in aqueous media, specifically for $SnCl_2$ [9]. When (40–50) wt% of ChCl is added to the water, $SnCl_2$ can be completely dissolved in it due to the good interaction between ChCl and Sn^{II} ion and the formation of complex as found in other Lewis acid metal chlorides/ChCl systems [10,11]. Co-impregnation of $AlCl_3$-ChCl on silica was also demonstrated as an effective Lewis acid solid catalyst for dehydration of carbohydrates to 5-hydroxymethylfurfural (HMF) [12]. In this study, $SnCl_2$/ChCl aqueous solution was used as the precursor for immobilization of Sn species on β-zeolite. It is expected to obtain high performance Sn-β-zeolite catalyst for glucose-fructose isomerization reaction.

2. Experimental

2.1. Materials

Glucose (98%), fructose (99%), mannose, dihydroxyacetone (dimer form) (DHA), lactic acid (LacA) (L-form, (85–92)%), formic acid (FA) (99.5%), levulinic acid (LevA) (95%), 5-hydroxymethylfurfural (HMF), Choline chloride (ChCl) (95%), tin(II) chloride ($SnCl_2$) (97%), tin(IV) chloride pentahydrate ($SnCl_4\cdot5H_2O$) (98%), isopropanol (99.7%), tin(IV) oxide (SnO_2) (98%) were purchased from WAKO Chemicals. High-silica β-zeolite with Si/Al ratio = 1700 in protonic form (HSZ-990 HOA) was obtained from Tosoh Corp. Distilled water was used in all experiments.

2.2. Catalyst preparation

Here, $SnCl_2$, which is very easy to precipitate as (hydr)oxides in the presence of water, was selected as the precursor to identify the advantage of the present method. Meanwhile, $SnCl_4$ was also used for comparison. Firstly, $SnCl_2$ was added into 20 mL of ChCl aqueous solution (50 wt%) and stirred until a homogeneous solution was obtained. Subsequently, 10 g of zeolite was added and stirred at room temperature for 12 h. Thereafter, the liquid was separated by filtration, and the obtained sticky gel was washed with isopropanol using Soxhlet apparatus for at least 2 h and then, dried at 50 °C for overnight. The obtained solid material is called as *x*Sn-βZ-UC, in which *x* represents the loading amount of tin (in this study, *x* = (0.6, 1.3, 1.9, 3.1 and 6.3) wt%). Furthermore, calcination was conducted in air at 550 °C for 6 h with a heating rate of 2 °C/min. The obtained powder is called as *x*Sn-βZ-C. Here, the parent β-zeolite was prepared by direct calcination of the commercial zeolite at the same conditions.

2.3. Catalyst characterization

Crystalline X-ray diffraction (XRD) patterns were checked on X-ray Rigaku diffractometer (Smartlab, Rigaku, Japan) using Cu K_α radiation source (λ = 1.5405 Å). Diffuse reflectance UV-visible (DRUV) was recorded on a JASCO V-650 spectrophotometer using ISV-722 integrating spheres coated with $BaSO_4$. Before measurement, the sample was vacuum-dried at 90 °C for overnight. Meanwhile, Fourier Transform Infrared (FTIR) spectra were obtained by using JASCO FT/IR-4200 infrared spectrophotometer with wavenumber in the range of 500–4000 cm^{-1}. In this context, the sample was mixed with KBr followed by pressing the mixture into thin pellet. To check the total acidity value, NH_3-temperature program desorption (NH_3-TPD) was conducted (Belcat, Japan) according to the reported procedure [13]. Surface morphology of materials were observed with a scanning electron microscope (SEM, SU8010, Hitachi, Japan) while transmission electron microscope (TEM) images were obtained using a JEM-2100F transmission electron microscope JEOL operating at 200 kV. ICP-OES measurement was performed using a Perkin Elmer Optima DV 7000 at 189.927 nm for Sn.

2.4. Chemical reaction

Reaction was performed in an autoclave reactor (Berghof, Germany). About 5 wt% of substrate was added into 10 mL of water containing 1 wt% of catalyst. The mixtures were heated and stirred at several operation conditions. After finished, the products were separated and analyzed using a Shimadzu Prominence HPLC according to our previous protocols [9]. In brief, the liquid product was filtrated using cellulose acetate membrane filter (0.2 μm) prior injected into HPLC. RID-10A (Shimadzu) and Supelcogel C610-H (30 cm × 7.8 mm) (Sigma) were used as the detector and the column, respectively. The oven CTO-20A was operated at 40 °C and H_3PO_4 (0.05%) was selected as the eluent.

3. Results and discussion

3.1. Catalyst synthesis and characterization results

Fig. 1(a) shows the XRD patterns of all the materials. Although the treated zeolites still conserved β-topology pattern, the diffraction peaks were shifted to the low angle when compared with the parent one, implying the changes of their structures to some extent. Interestingly, the peaks at 2θ values of 13.5° and 14.8° were disappeared while some new peaks (*i.e.* at 2θ values of 16.9°, 17.2°, 18.6°, 22.2°, 28.5° and 29.3°) were observed on 1.3Sn-βZ-UC. However, it should be noted that the peaks at 13.5° and 14.8° reappeared while those new peaks vanished again after calcination, indicating the presence of crystalline organic substance on zeolite before calcination. The new XRD peak of 1.3Sn-βZ-UC at 29.3° was confirmed as the main diffraction of ChCl. Furthermore, FTIR results suggested that ChCl was immobilized at first, and then removed after heated (Fig. 1(b)). Herein, the existence of ChCl after using 1.3Sn-βZ-UC was also detected in the product by HPLC. On the other hand, owing to the ability of ChCl to form Lewis-acidic ionic complexes with $SnCl_2$ [14], it can assist tin species to well disperse into zeolite. At this state, it is found that no significant loss of Sn observed in the liquid after reaction by ICP measurement. Noted, the similar phenomenon has also reported by Yang *et al.* [12] for silica-based catalyst. In this context, the calcination facilitated tin species to get into the framework of zeo-

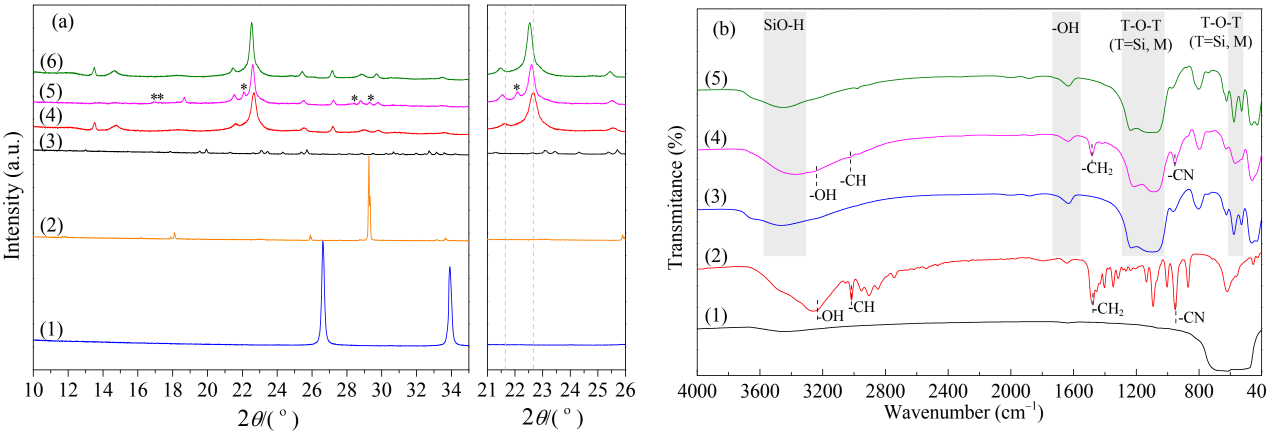


Fig. 1. (a) XRD patterns of SnO_2 (1), crystalline ChCl (2), $SnCl_2$ (3), parent β-zeolite (4), 1.3Sn-βZ-UC (5) and 1.3Sn-βZ-C (6). The appearances of new peaks are marked as a star point. (b) FTIR spectra of SnO_2 (1), ChCl (2), parent β-zeolite (3), 1.3Sn-βZ-UC (4) and 1.3Sn-βZ-C (5). *x*Sn indicates the loading amount value in wt% unit.

lite as indicated from the shifting peaks of XRD as well as the typical signal of DRUV spectra. Meanwhile, the typical diffraction of SnO_2 was not observed for all treated zeolites, indicating the effectiveness of this method to prevent the hydrolysis of tin into (hydr)oxides [7,9] or other polymeric substances [4] during the treatment and thus minimizing the formation of unwanted tin species. However, it should be noted that the existence of some aggregates of Sn-O-Sn or other tin species was not hindered which were indicated from the DRUV spectra as well as TEM images. Detail explanations will be presented further in the following section.

DRUV measurement was carried out as one of common tools to get qualitative assessment of tin species on zeolite [1,4,15,16] and the results are depicted in Fig. 2(a, b). To make Sn state more clearly, the spectra of Sn-ChCl-treated zeolites were corrected with the ChCl-treated zeolite without Sn loaded (notified as 0Sn-βZ) (Fig. 2(b)). It can be seen that the peak at 200 nm, assigned to the Sn in the tetrahedrally coordinated framework [1,15,16], was observed and increased aligned with tin loading amount on zeolite. Interestingly, in the case with low tin loading (*i.e.* <3.1 wt%), the different absorption band was observed in the region of 215–340 nm when compared with the parent one as well as the catalysts prepared in pure water (Fig. 2(a)), and it was similar with that of 0Sn-βZ catalyst, indicating that neither the tin oxide nor other tin species affected this absorption. Recently, it is reported that the intercalation of choline followed by calcination can favor the desired 'shifted' orientation structure of IPC-1P zeolite, a kind of layered structure material, and produce new 'unfeasible' structure of zeolite [17]. Moreover, it also promoted dealumination process which affected the acidity of zeolite, indicating the great interaction between choline and silanol group in zeolite. In this study, the decrease in acidity was observed from the NH_3-TPD analysis result of 0Sn-βZ zeolite (Fig. 5), also indicating the possible occurrence of this phenomena. Considering these results, immobilization of ChCl followed by calcination can change the silica structure of β-zeolite, which opens a new way to incorporate tin into the zeolite.

For comparison, loading of tin was also performed in pure water. As expected, the DRUV absorption pattern was totally different from those of ChCl-treated zeolite as well as the parent one (Fig. 2(a)). Although no obvious peaks of SnO_2 were observed on XRD patterns (Fig. 2(c)), DRUV spectra showed low signal and the broad band at 200 and 260 nm, respectively, indicating the formation of other inactive tin species besides the isolated form. For example, the signals in the range of 240–350 nm should be assigned as the typical absorption of oligomeric tin compounds [5]. Specifically, the extraframework and polymeric Sn-O-Sn always had the high absorption peaks in the ranges of 255–260 nm [4,5,18], and 270–280 nm [4,15,18],

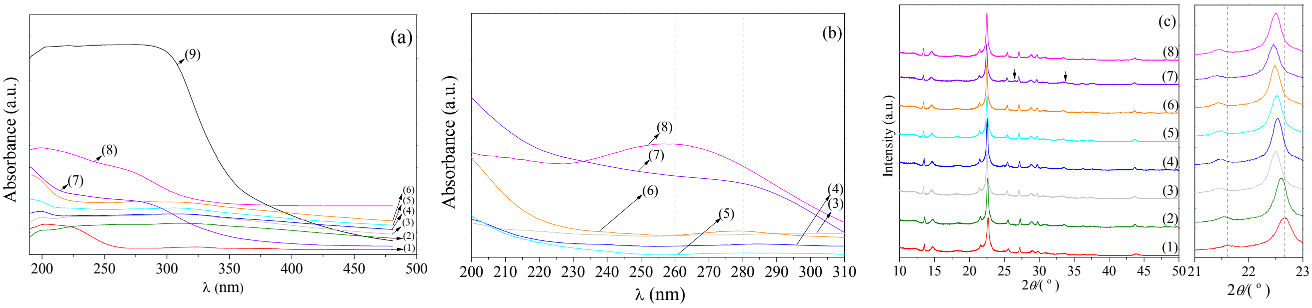


Fig. 2. DRUV spectra (a, b) and XRD patterns (c) of parent (1) compared with ChCl-treated zeolite with different loading amounts of Sn (wt%): 0 (2), 0.6 (3), 1.3 (4) 1.9 (5) 3.1 (6) 6.3 (7), H_2O-prepared zeolite with 1.3 wt% of Sn (8) and SnO_2 (9). (b) is obtained after corrected with the ChCl-treated zeolite without the addition of Sn. The appearance of SnO_2 diffraction peak on (c) is showed by the arrow.

respectively. The peaks on the latter range were considered from the hydrated form of tin or even octahedral extraframework SnO_2 [4,5,18]. The absorption band at 260 nm should be correlated with the precipitation of Sn^{2+} ions soon after the salt was added in pure water, i.e., the hydrolysis to (hydr)oxides [7], and as such, the agglomeration should occur, which was supported by the TEM images (Fig. 3(c) and (d)). On the other hand, it is found that the good solubility of $SnCl_2$ in ChCl solution can minimize the formation of those inactive species as long as the amount of tin was lower than 3.1 wt% in this study. Other works reported that the solubility of tin had great responsibility to the morphology as well as the catalytic activity of tin-β-zeolite prepared via hydrothermal route [19]. Moreover, the isolated tin species in the framework were difficult to be formed when performing the grafting in pure water [5].

As shown in Fig. 3(c), Sn species were dispersed with random sizes on zeolite when Sn-β-zeolite was prepared in pure water without ChCl. Moreover, some Sn particles were obviously observed on the surface of zeolite (Fig. 3(d)), indicating the agglomeration of tin species which typical DRUV absorption signals have been discussed above. On the contrary, smaller and more uniform Sn particles were found to be well dispersed on zeolite when Sn-β-zeolite was prepared in the ChCl aqueous solution (inset of Fig. 3(b)). It is indicated that the formation of other tin species besides isolated form could be suppressed although a small aggregate could not be hindered even at this state. Thus, maintaining tin solubility in the solvent should be considered strictly to obtain Sn-β-zeolite with well metal dispersion. These results indicated that the performing of stannation through the present route can result in a very well dispersion of tin on zeolite.

On the other hand, when Sn loading amount was over 3.1 wt%, as shown in Fig. 2, it is found that the peak at around 270–280 nm was observed on DRUV spectrum. Moreover, a broad peak at around 280 nm, which corresponds to the typical SnO_2 species, appeared when the Sn loading amount was 6.3 wt%. It was also supported by SEM images, on which some disordered bright objects were observed (Fig. 4), indicating that some SnO_2 formed on the outside of zeolite as also found by others [5]. As reported by others [1,3,5], in this study, 5 wt% loading amount seemed to be the limit amount to prevent the formation of such inactive tin species.

Fig. 5 shows NH_3-TPD profiles of parent zeolite and Sn-β-zeolite prepared in ChCl aqueous solutions with different tin loading amounts. Since the parent one was a protonic form of β-zeolite with low aluminum content as the Lewis acid source, it had low total acidity value. With the increase in tin loading amount, the acidity was also increased. Here, the high intensity peak at around 205–225 °C indicates the presence of Lewis acid sites [20,21], which also indicated the total acidity value of the prepared Sn-β-zeolite. In this context, Lewis acid sites from tin species should have great contribution to the obtained value. One can see that the acidity decreased to some extent after the zeolite was only treated with ChCl, which should be resulted from the great interaction between choline and silanol bonds in the zeolite [17].

3.2. Catalytic Activity

Table 1 shows the catalytic activity of the prepared

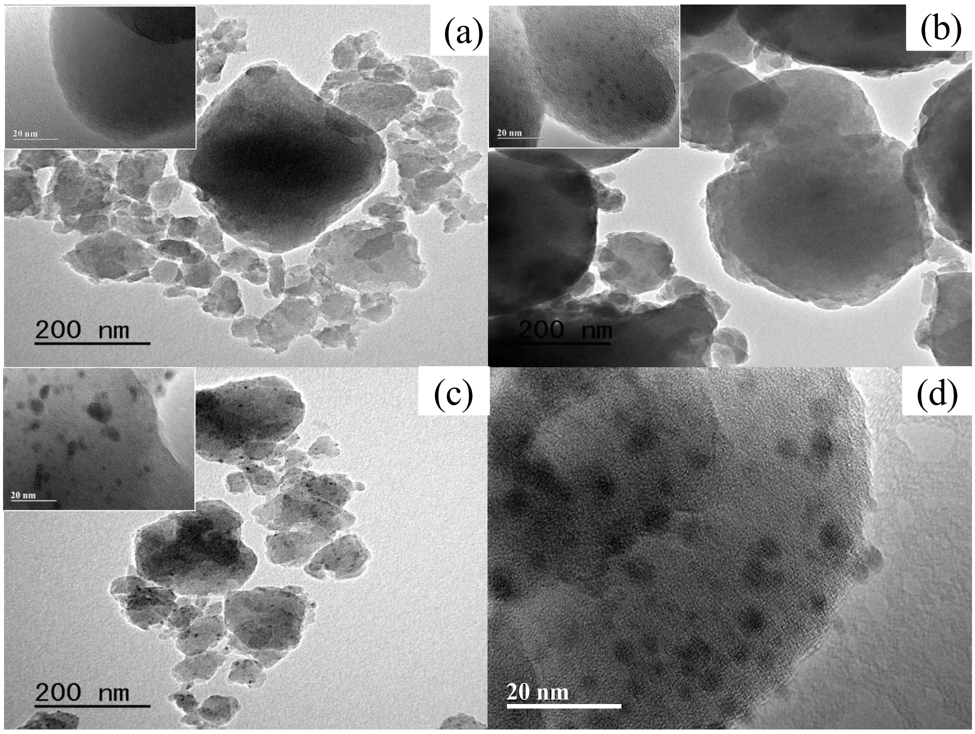


Fig. 3. TEM images of parent β-zeolite (a), 1.3Sn-βZ-C prepared in ChCl solution (b) and in pure water (c, d).

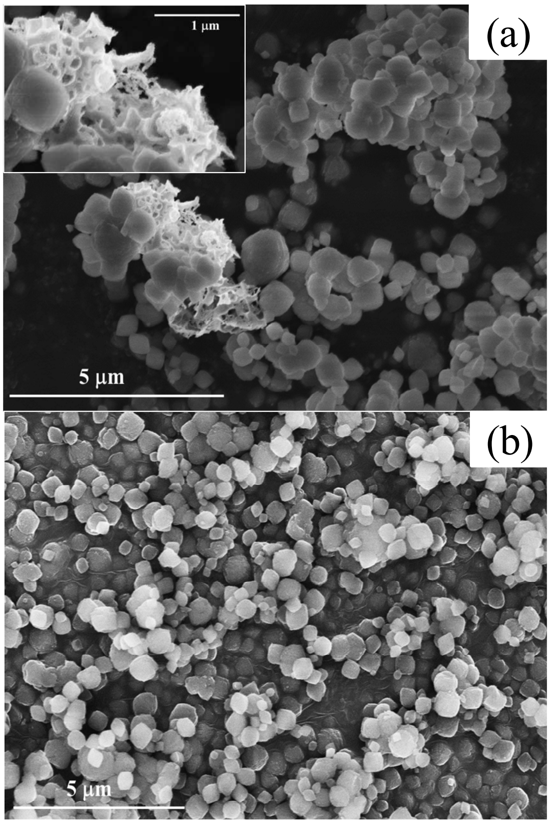
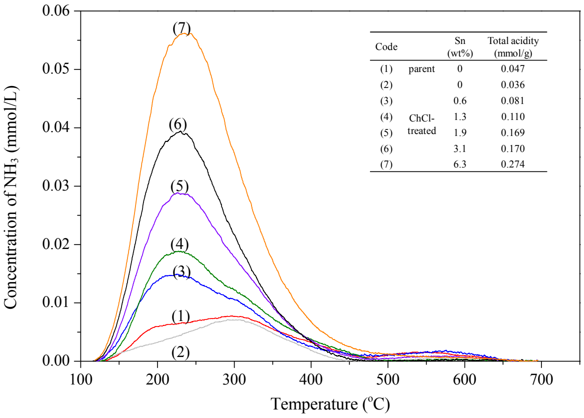


Fig. 4. SEM images of 6.3Sn-βZ-C (a) and 1.3Sn-βZ-C (b).



Code		Sn (wt%)	Total acidity (mmol/g)
(1)	parent	0	0.047
(2)	ChCl-treated	0	0.036
(3)		0.6	0.081
(4)		1.3	0.110
(5)		1.9	0.169
(6)		3.1	0.170
(7)		6.3	0.274

Fig. 5. NH_3-TPD profiles of parent zeolite (1) and Sn-β-zeolite prepared in ChCl aqueous solutions with different tin loading amounts (2–7).

Sn-β-zeolite for aqueous hexoses conversion reaction. One can see that the parent β-zeolite had very low performance due to its low acidity, especially the Lewis acid site (Table 1, entry 1). After Sn loading, the activity increased either with or without calcination (Table 1, entries 3 and 2, respectively). However, the calcination seemed to have a great effect to induce the generation of Sn active sites in β-zeolite while $SnCl_2$/ChCl played an important role in improvement of the catalytic performance in the case without calcination. In our previous work, $SnCl_2$/ChCl was found to have high activity for aqueous catalytic reaction of glucose [9]. For comparison, the catalytic activity of Sn-β-zeolite prepared in pure water was also investigated. It had lower activity than those prepared in ChCl aqueous solutions (Table 1, entries 8 and 9) due to the low Sn content on it based on ICP measurement (*i.e.* (0.13 and 0.40) wt%, respectively). However, it showed high selectivity for fructose formation, indicating that different active species should be formed as discussed above. These results identified that the catalytic activity of Sn-β-zeolite should be related with the presence of active sites of tin as the Lewis acid, especially in its isolated form.

The prepared catalysts were also used for the conversions of other hexoses in this study. When fructose was used as the substrate, a large amount of glucose was found to be produced (Table 1, entry 4) since this reaction is an equilibrium reaction [22,23]. This result indicates that this catalyst is benefit for the glucose-fructose isomerization reaction as typically observed for the common Sn-β-zeolite [4,22]. It is supported from the high selectivity fructose formation when reaction was carried

Table 1

Catalytic performance for hexoses conversion reaction in aqueous solutions.

Entry	Hexoses	Catalyst	*T* (°C)	Conv. (mol%)	Yield (mol%) Gluc	Fruc	DHA	LacA	HMF	Selectivity [a] (%)
1	Gluc	Parent	145	9.5		2.5	—	—	—	26
2	Gluc	1.3Sn-βZ-UC	145	30.5		15.7	<1	—	—	51
3	Gluc	1.3Sn-βZ-C	145	72.1		41.4	1.5	5.5	3.9	57
4	Fruc	1.3Sn-βZ-C	145	55.4	17.8		1.6	9.2	7.8	
5	Gluc	1.3Sn-βZ-C	125	58.6	—	46.3	1	4.1	<1	79
6 [b]	Gluc	1.3Sn-βZ-C	125	54.6	—	47.1	<1	2.0	<1	86
7	Mann	1.3Sn-βZ-C	125	36.0	18.8	—	1.7	5.1	—	
8 [c]	Gluc	1.3Sn-βZ-C	125	19.2		16.0	—	—	—	83
9 [c]	Gluc	1.3Sn-βZ-C	145	30.3		22.9	—	—	—	76
10 [d]	Gluc	1.3Sn-βZ-C	125	35.8		30.2	<1	<1	—	84
11 [d]	Gluc	1.3Sn-βZ-C	145	57.4		37.3	<1	4.3	3.3	65
12 [c,d]	Gluc	1.3Sn-βZ-C	125	19.5		11.9	—	—	—	61
13 [c,d]	Gluc	1.3Sn-βZ-C	145	25.3		17.2	—	—	—	75

Reactions: 5 wt% of hexoses, 1 wt% of catalyst, 10 mL of water, 1.5 h in autogenous state. Gluc, Fruc, Mann, *T*, and Conv. are the abbreviations of glucose, fructose, mannose, reaction temperature and conversion, respectively.

[a] For fructose formation; [b] after 1 h of reaction time; [c] prepared in pure water; [d] using $SnCl_4$ as the precursor in equimolar condition.

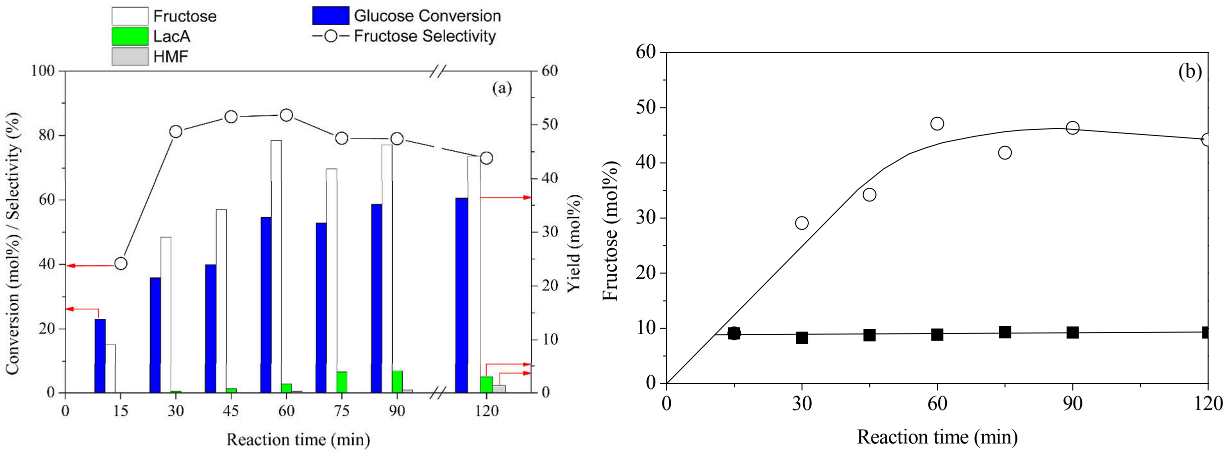


Fig. 6. Product evolution (a) and heterogeneity test (b) for aqueous glucose conversion using 1.3Sn-β-zeolite. Reactions: 5wt% of glucose, 1 wt% of catalyst, 10 mL of water at 125 °C. Heterogeneity test was conducted based on the reported protocol [4].

out at low reaction temperature (Table 1, entry 5 and 6). In this case, about (45–47)% of fructose was obtained after 60–90 min of reaction (Fig. 6(a)). With further extending of the reaction time, the yield and selectivity decreased slightly and other products such as HMF were observed in significant amounts, indicating that fructose was further transformed to other side products. In this context, as shown in Fig. 6(b), it is obviously observed that the reaction occurred via heterogeneity state of zeolite.

Meanwhile, a significant amount of glucose was obtained from mannose by using this Sn-β-zeolite (Table 1, entries 7). In contrast with other results [4], mannose was not detected in the product obtained from glucose as the substrate, presumably small peak of mannose could not be detected in our HPLC condition since it has a close retention time as that of fructose (*i.e.* 11.53 and 11.60 min, respectively). Considering its low activity for glucose-mannose reaction in the case without some additives [24] and its good ability for glucose-fructose reaction [4], it is hypothesized that the nature of β-topology of zeolite and the isolated tin active sites on it have great contribution to the isomerization of glucose to fructose rather than epimerization reaction. In this context, since these reactions generally occur competitively [24], glucose isomerization seems to be more preferable to occur due to the high energy barrier of the latter reaction. It should be noted that intramolecular 1,2-hydride shift [23] and 1,2-carbon shift [24] could happen for the isomerization and epimerization, respectively, which have different thermodynamical activation energy.

Since tin chlorides are available in two forms of oxidation state, Sn-β-zeolite was also prepared by using $SnCl_4$ as the precursor. It is found that the obtained catalysts had lower activity than those obtained from immobilization of $SnCl_2$ (Table 1, entries 10,11 and 3,5, respectively). It is possible that the two kinds of tin chlorides have different interactions with ChCl, which affect Sn dispersion during the loading process. ICP measurement confirmed the different tin contents observed for both catalysts (*i.e.* (0.24 and 0.40) wt%, respectively). Here, the $SnCl_2$ is able to form an eutectic salt with ChCl [14], however, such a complex was not commonly reported for $SnCl_4$. Furthermore, a higher selectivity for fructose formation and a higher TOF_{Sn} value were found for $SnCl_4$ than $SnCl_2$ (*i.e.* 265–331 and 228–255 h^{-1}, respectively) indicated that the oxidation state of Sn also contributed to the Sn active site formation during the calcination step. In this study, the variation of Sn precursor clearly showed that different precursors have different interaction with zeolite framework, which affected the physical and catalytic behaviors of the obtained Sn-β-zeolites as prepared via alcoholic grafting method [5]. Meanwhile, performing stannation in pure water with $SnCl_4$ also resulted in higher TOF_{Sn} when compared with $SnCl_2$ (*i.e.* 281 and 274 h^{-1} at 125 °C for 1.5 h, respectively), indicating the possible different Sn dispersions as well as active forms on zeolite. As described above, white precipitate appeared shortly after adding $SnCl_2$ into pure water, however, such phenomenon was not soon observed in the case of $SnCl_4$, where white suspension appeared after storing the solution for 2 days, indicating its lower hydrolysis rate than $SnCl_2$. Therefore, considering these results and other reports [5], the solubility or choosing an appropriate solvent for tin salts should be important for the preparation of Sn-β-zeolite with high performance.

The catalytic activity of catalyst with different tin loading amounts was also investigated. Although the yields of fructose as well as the conversion value were not significantly different, side products such as FA as well as HMF were significantly formed when the Sn loading amount was increased. Moreover, LacA was also detected and increased slightly, confirming the existence of other reactions besides glucose-fructose isomerization. As indicated above, more other tin species were possibly formed at high Sn loading amounts. Since the speciation of tin species on zeolite (*e.g.* isolated or extraframework) could affect the activity as well as selectivity [15], other side reactions could be catalyzed by them so that other products were detected as shown in Fig. 7. Considering of these results, 1.3 wt% of tin loading amount should be the optimum one for the aqueous glucose-fructose isomerization reaction.

The reusability of the prepared catalyst was also investigated. Relative activity is used to see the catalytic performances of the reused as well as recycled catalyst compared with the

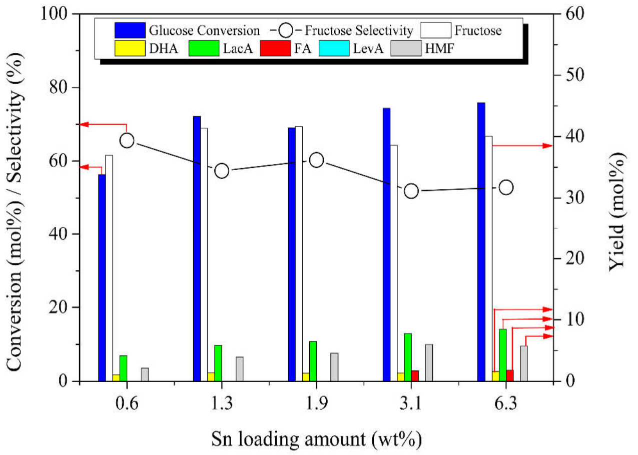


Fig. 7. Effect of Sn loading amount on the catalytic activity of Sn-β-zeolite. Reactions conditions: 5 wt% of glucose, 1 wt% of catalyst, 145 °C.

fresh one. It is found that the activity of catalyst decreased to some extent (Fig. 8) and the color changed to brown after reused, indicating the loss of activity due to the existence of some impurities formed on the catalyst. These impurities could cover the active sites of the catalyst, and lower its activity. After the spent catalyst was calcined and reused, as shown in Fig. 8, the activity recovered to some extent but was still lower than the fresh one. It is possible that some active sites were lost and/or the structure was changed as reported by others [25]. ICP measurement confirmed that some amount of tin (*i.e.* ~1 wt%) was lost from the fresh catalyst. However, it should be noted that the selectivity for fructose formation remained relatively constant.

4. Conclusions

Immobilization of $SnCl_2$/ChCl into high-silica commercial β-zeolite followed by calcination was identified as an effective way to prepare well Sn dispersed zeolite catalysts. 1.3 wt% of Sn loading amount was found to be the optimum one, in which not only well dispersion of Sn species was realized but also less inactive tin species were formed on zeolite. The obtained Sn-β-zeolite shows good catalytic activity as well as selectivity for aqueous glucose-fructose isomerization reaction. The present method should be a novel alternative process for preparing Sn loaded catalyst with high performance.

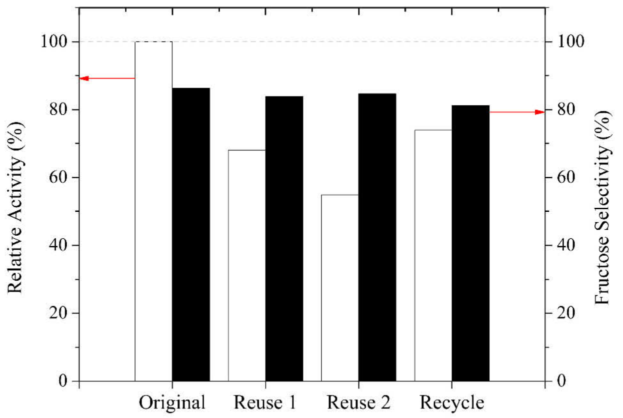


Fig. 8. The reusability of 1.3Sn-βZ-C in aqueous glucose conversion. Recycle test was performed after calcining the zeolite from reuse 2. Reaction conditions: 5 wt% of glucose, 1 wt% of catalyst, 125 °C.

References

[1] P. Li, G. Q. Liu, H. H. Wu, Y. M. Liu, J. G. Jiang, P. Wu, *J. Phys. Chem. C*, **2011**, 115, 3663–3670.

[2] C. Hammond, S. Conrad, I. Hermans, *Angew. Chem. Int. Ed.*, **2012**, 51, 11736–11739.

[3] C. Hammond, D. Padovan, A. Al-Nayili, P. P. Wells, E. K. Gibson, N. Dimitratos, *ChemCatChem*, **2015**, 7, 3322–3331.

[4] J. Dijkmans, D. Gabriels, M. Dusselier, F. de Clippel, P. Vanelderen, K. Houthoofd, A. Malfliet, Y. Pontikes, B. F. Sels, *Green Chem.*, **2013**, 15, 2777–2785.

[5] J. Dijkmans, J. Demol, K. Houthoofd, S. G. Huang, Y. Pontikes, B. F. Sels, *J. Catal.*, **2015**, 330, 545–557.

[6] P. Y. Dapsens, C. Mondelli, J. Perez-Ramirez, *New J. Chem.*, **2016**, 40, 4136–4139.

[7] M. Dusselier, P. Van Wouwe, A. Dewaele, E. Makshina, B. F. Sels, *Energy Environ. Sci.*, **2013**, 6, 1415–1442.

[8] P. Y. Dapsens, C. Mondelli, J. Perez-Ramirez, *Chem. Soc. Rev.*, **2015**, 44, 7025–7043.

[9] A. Bayu, G. Q. Guan, S. Karnjanakom, X. G. Hao, K. Kusakabe, A. Abudula, *Chem. Select*, **2016**, 1, 180–188.

[10] F. Liu, M. Audemar, K. De Oliveria Vigier, D. Cartigny, J. M. Clacens, M. F. Costa Gomes, A. A. H. Padua, F. De Campo, F. Jerome, *Green Chem.*, **2013**, 15, 3205–3213.

[11] P. De Vreese, N. R. Brooks, K. Van Hecke, L. Van Meervelt, E. Matthijs, K. Binnemans, R. Van Deun, *Inorg. Chem.*, **2012**, 51, 4972–4981.

[12] J. Yang, K. D. O. Vigier, Y. L. Gu, F. Jerome, *ChemSusChem*, **2015**, 8, 269–274.

[13] S. Karnjanakom, A. Bayu, P. Xiaoketi, X. G. Hao, S. Kongparakul, C. Samart, A. Abudula, G. P. Guan, *RSC Adv.*, **2016**, 6, 50618–50629.

[14] A. P. Abbot, G. Capper, D. L. Davies, H. L. Munro, R. K. Rasheed, V. Tambyrajah, *Chem. Commun.*, **2001**, 2010–2011.

[15] R. Bermejo-Deval, R. Gounder, M. E. Davis, *ACS Catal.*, **2012**, 2, 2705–2713.

[16] H. Y. Luo, J. D. Lewis, Y. Roman-Leshkov, *Annu. Rev. Chem. Biomol. Eng.*, **2016**, 7: 663–692.

[17] M. Mazur, P. S. Wheatley, M. Navarro, W. J. Roth, M. Polozij, A. Mayoral, P. Eliasova, P. Nachtigall, J. Cejka, R. E. Morris, *Nat. Chem.*, **2016**, 8, 58–62.

[18] J. Dijkmans, M. Dusselier, D. Gabriels, K. Houthoofd, P. C. M. M. Magusin, S. G. Huang, Y. Pontikes, M. Trekels, A. Vantomme, L. Giebeler, S. Oswald, B. F. Sels, *ACS Catal.*, **2015**, 5, 928–940.

[19] S. Tolborg, A. Katerinopoulou, D. D. Falcone, I. Sadaba, C. M. Osmundsen, R. J. Davis, E. Taarning, P. Fristrup, M. S. Holm, *J. Mater. Chem. A*, **2014**, 2, 20252–20262.

[20] M. Casagrande, E. Moretti, L. Storaro, M. Lenarda, J. Gersich, L. Stievano, F. E. Wagner, *Micropor. Mesopor. Mater.*, **2006**, 91, 261–267.

[21] P. Y. Dapsens, C. Mondelli, J. Perez-Ramirez, *ChemSusChem*, **2013**, 6, 831–839.

Graphical Abstract

Chin. J. Catal., 2017, 38: 426–433 doi: 10.1016/S1872-2067(17)62754-2

Preparation of Sn-β-zeolite via immobilization of Sn/choline chloride complex for glucose-fructose isomerization reaction

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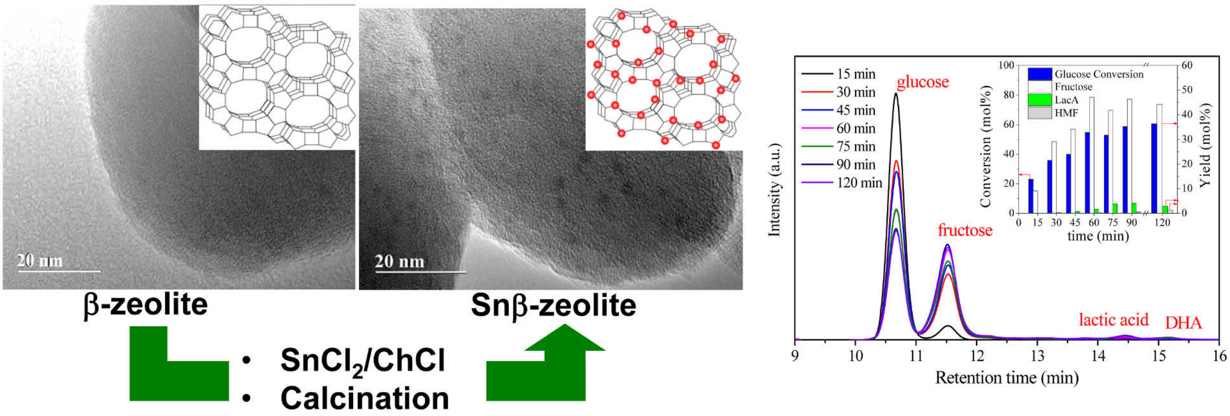

Sn-β-zeolite prepared by immobilization of SnCl$_2$/ChCl followed by calcination showed good activity and high selectivity for glucose-fructose isomerization.

[22] M. Moliner, Y. Roman-Leshkov, M. E. Davis, *PNASUSA*, **2010**, 107, 6164–6168.

[23] Y. Roman-Leshkov, M. Moliner, J. A. Labinger, M. E. Davis, *Angew. Chem. Int. Ed.*, **2010**, 49, 8954–8957.

[24] W. R. Gunther, Y. R. Wang, Y. W. Ji, V. K. Michaelis, S. T. Hunt, R. G. Griffin, Y. Roman-Leshkov, *Nat. Commun.*, **2012**, 3, 1109.

[25] G. M. Lari, P. Y. Dapsens, D. Scholz, S. Mitchell, C. Mondelli, J. Perez-Ramirez, *Green Chem.*, **2016**, 18, 1249–1260.