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Short Communication

Efficient and selective conversion of hexose to 5-hydroxymethylfurfural with tin–zirconium-containing heterogeneous catalysts

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Efficient and selective production of 5-hydroxymethylfurfural (HMF) from the hexose is achieved in the presence of heterogeneous Sn-based catalyst. The mixed SnO_2–ZrO_2 is prepared from zirconium n-propoxide and different metal Sn precursors using Sol–gel method. The sulfated SnO_2–ZrO_2 (SO_4^{2-}/SnO_2–ZrO_2) is obtained by the impregnation method with H_2SO_4 solution. All catalytic materials are detected with XRD, TG, SEM, TEM and BET techniques in order to reveal the physical properties and structures of these materials. When these materials were used in the dehydration of fructose, it was found that the suitable ratio of Sn/Zr is 0.5, and the catalytic activity of SO_4^{2-}/SnO_2–ZrO_2 is higher than that of SnO_2–ZrO_2 where more than 75.0% yield of HMF was obtained for 2.5 h at 120 °C. The effects of reaction temperature and reaction time were also investigated. Moreover, the recycling experiment of catalyst shows that the catalytic activity can be almost kept unchanged after being used five times.

1. Introduction

In the past decades, fossil resources containing oil, natural gas and coal had been considered as the important origins of energy and high-value fine chemical; however, along with the increasingly environmental pollution and energy crises in recent years, renewable biomass feedstock and its further applications have attracted many scientists' great attentions [1,2]. In chemistry field, an increasing effort has been devoted to the catalytic transformation of biomass resources to the value-added fine chemicals and biofuels [3–5]. As a potential alternative route, the selective conversion of sugars to valuable chemicals become more and more important in the chemical processing from biomass resources. Therein, the production of furans from carbohydrates has been broadly studied [6], in which 5-hydroxymethylfurfural (HMF), a dehydration production of hexoses, is one of the important chemical intermediates and platform chemicals [7]. Considering the molecular structure, HMF is often used for preparing high density liquid fuel 2,5-dimethylfuran (DMF) or polymeric monomer furan-2,5-dicarboxylic acid (FDCA) as the raw material [8,9]. Also, the HMF had great potential to serve as a substitute for the preparation of non-petroleum-derived building blocks that were used in the production of polyamide and more fine products [10]. Thus, developing a novel and efficient catalytic system for the dehydration of sugars to HMF has gradually been a hot topic [11].

Using liquid acids as catalysts, various researches have been performed on the catalytic dehydration of different hexoses [3,12–14]. Therein, Antal and Mok [12] reported the catalytic dehydration of fructose with H_2SO_4 as a catalyst in the subcritical water at 250 °C, and a 53% yield of HMF was gained. Domestic's group reported the production of HMF from D-fructose in a biphasic reactor system, in which hydrochloric acid was employed as the catalyst and MIBK–2-butanol mixture was chosen as organic phase. After optimization, the selectivity of HMF could reach 89% at high fructose conversion [3,13]. Furthermore, a HMF yield of 60% was achieved at 92% fructose conversion and a HMF selectivity of 65% using $B(OH)_3$ and sodium chloride as catalyst in the aqueous phase and methyl-isobutylketone (MIBK) as extracting solvent [15]. Except for inorganic acids, metal halides were also employed as the catalysts for the production of HMF [16–23]. For example, $CrCl_2$ is found to be uniquely effective in 1-alkyl-3-methylimidazolium chloride, leading to the conversion of hexoses to HMF with a yield over 70% [16]. Moreover, Yong et al. [17] found that more than 81% yield of HMF was respectively achieved in the dehydration of hexoses with a NHC–Cr/ionic liquid system at 100 °C for 6 h in the air. Also, Seri et al. [18] found that lanthanide (III) could efficiently catalyze the dehydration of hexoses to HMF in H_2O at 140 °C. Hu et al. [19] revealed that $SnCl_4$ could efficiently promote the conversion of hexoses to HMF in $[BMIM]BF_4$ ionic liquid and the yield is as high as 61%. Furthermore, our group also reported that a combination of $FeCl_3$ and tetraethyl ammonium bromide is the efficient catalyst for the dehydration of fructose in which that about 86% HMF yield was achieved at full conversion of fructose [21]. We also found that a 73.8% yield of HMF from fructose and a 69.1% yield of HMF from glucose were obtained with $SnCl_4$ and tetrabutyl ammonium bromide in DMSO for 2 h at 100 °C [22].

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Compared to liquid acid catalysts and metal chlorides, the solid acid catalysts have the following advantages: (a) they facilitate the separation of product and can be recycled; (b) they can work at high temperatures, thus shortening the reaction time and favoring the formation of HMF instead of its decomposition during a prolonged reaction period; and (c) they are capable of adjusting the surface acidity to improve the selectivity of HMF, which will be very useful to the conversion of polysaccharides and biomass feedstocks [23]. Therein, the heterogeneous catalysts such as alumina [24], aluminosilicate [25], zirconium phosphate [26], niobic acid [27], ion-exchange resin Amberlyst-15 [28], and zeolite [29,30] have been investigated in the catalytic and selective conversion of different carbohydrates, and the promising results were gained. Very recently, a solid heteropolyacid $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ has been used as catalyst in the converting fructose to HMF, in which a 74.0% yield and 94.7% selectivity of HMF was obtained in 60 min at 115 °C [31]. Furthermore, Smith's group and Qi's group reported the dehydration of fructose to HMF with the sulfated zirconia under mild conditions. As a result, 72.8% or 88.4% yield of HMF in the high conversion was respectively obtained in acetone–dimethylsulfoxide mixtures [32] or 1-butyl-3-methyl imidazolium chloride [33]. Moreover, Ning et al. [34] reported that the yield of HMF could reach 86.5% in 1-ethyl-3-methylimidazolium bromide with tin(IV) phosphonate as the catalyst which was obtained from the reaction of $SnCl_4 \cdot 5H_2O$ and N,N-bis(phosphonomethyl) aminoacetic acid. However, these catalytic systems have some disadvantages: either the reaction is performed with expensive ionic liquids as the solvents, or the preparation of catalyst is complicate. Thus, developing the efficient and simple catalytic process for synthesis of HMF from carbohydrate keeps a challenge.

In the present study, we propose a new efficient preparation of HMF from hexoses with mixed SnO_2–ZrO_2 and SO_4^{2-}/SnO_2–ZrO_2 solid acid catalysts. These catalysts are prepared by Sol–gel method using $Zr(OC_3H_7)_4$ and dimethyltin dichloride $[Sn(CH_3)_2Cl_2]$ or tin(IV) chloride ($SnCl_4$) as the metal precursors. The selective and efficient conversion of fructose to produce HMF is achieved. Moreover, the effects of different Sn-based materials, reaction temperature and reaction time were investigated in detail.

2. Experimental section

2.1. Reagents

Fructose, glucose, $SnCl_4$, $Sn(CH_3)_2Cl_2$, deionized water, $Zr(OC_3H_7)_4$, ethanol, ammonia, sulfuric acid and silver nitrate are analytic grade and purchased from commercial sources. Dimethyl sulfoxide (DMSO), tetrahydrofuran (THF) and acetic ether ($CH_3COOC_2H_5$) were purified by distillation prior to use. The HMF as a standard sample in HPLC analysis is purchased from Alfa Aesar.

2.2. The preparation for catalyst

a) The synthesis of SnO_2–ZrO_2 catalytic materials: a certain amount of $Zr(OC_3H_7)_4$ and $Sn(CH_3)_2Cl_2$ or $SnCl_4$ were added into a 250 mL round bottomed flask, and then directly dissolved in anhydrous ethanol assisted by the ultrasonic agitation. In the following, NH_4OH–ethanol (1:1, v/v) solution was added dropwise into the above solution until the pH = 11. The mixture was stirred and heated at 83 °C with an oil bath and refluxed for 1.5 h until the corresponding colloidal were formed completely. In order to remove the left feedstock , the solid product was filtered and washed by distilled water, ethanol and ethyl acetate, respectively. Then, the obtained solid was dried at 100 °C overnight and calcinated at 550 °C for 4 h. Herein, the different catalysts with Sn/Zr = 0.1, 0.2, 0.03, 0.05 (g/g) from $Zr(OC_3H_7)_4$ and $Sn(CH_3)_2Cl_2$ are signified by DZ-1, DZ-2, DZ-03 and DZ-05, respectively. The catalyst from $Zr(OC_3H_7)_4$ and $SnCl_4$ with Sn/Zr = 0.05 is represented by TZ-05. The uncalcinated catalysts are signified by n-DZ-05 and n-TZ-05.
b) Synthesis of sulfated SnO_2–ZrO_2 (SO_4^{2-}/SnO_2–ZrO_2): the prepared DZ-05 and TZ-05 are respectively placed in 1 M H_2SO_4 solution and kept for 12 h under stirring. Then the obtained solid is further dried at 100 °C overnight. Herein, sulfated SnO_2–ZrO_2 from DZ-05 and TZ-05 is written as SDZ-05 and STZ-05.

2.3. Catalyst characterization

The measurement of X-ray diffraction (XRD) was performed by diffractometer with Cu Ka radiation source at 35 kV, 40 mA (0.02° resolution) and was collected from 10 to 80° [2θ]. The morphology of catalytic materials was obtained by a scanning electron microscope (SEM: JSM-6301F, JEOL) and a transmission electron microscope (TEM: JEM-2100, JEOL). BET surface areas, pore volumes, and average pore diameters of the prepared samples were obtained from N_2 (77 K) adsorption measurement using a Micromeritics ASAP2020M system. Therein, the samples were pretreated under vacuum at 250 °C for 4 h before the measurement. The average pore diameter data were calculated according to the Barrett–Joyner–Halenda (BJH) model in absorption and desorption period.

2.4. General procedure for the dehydration of fructose and the product analysis method

All the dehydration reaction experiments were performed in a 100 mL autoclave equipped with magnetic stirring and a temperature controller. Herein, a typical step on dehydration of fructose is given in the following: 1.0 g fructose, 0.1 g catalyst and 10 mL solvent were added in order after the air in autoclave is replaced with nitrogen for three times. Then, the autoclave is sealed, and the mixture was stirred and preheated to 100 °C. Next, the reaction temperature was kept for 100 min. When the reaction was finished, the mixture was transferred to a volumetric flask. The products were diluted with anhydrous ethanol. The yield of HMF was obtained based on the analysis by HPLC with external standard method.

The quantitative analysis of the products was performed on a Cometro 6000 equipped with LDI pump and PVW UV detector. Chromatographic column type is Kromasil, C18, 5 μ, 250 × 4.6 mm. Qualitative analysis is carried on the Agilent 6890/5973 GC–MS. The NMR spectra are recorded on an INOVA 500 MHz spectrometer.

2.5. Separation of the product 5-hydroxymethylfurfural (HMF)

After the dehydration of fructose, the mixture was added into a saturated aqueous $NaHCO_3$ solution and stirred with a magnetic stirrer overnight. The product was extracted four times with $CH_3COOC_2H_5$. The organic phase was collected and dried with anhydrous sodium sulfate. The organic layer was distilled under reduced pressure to obtain pure HMF as a main product. ^1H NMR spectrum (DMSO-d_6): 3.396–3.438 (d, 1H, J = 7.078), 4.483 (s, 2H), 6.580–6.586 (d, 1H, J = 3.417) 7.466–7.473 (d, 1H, J = 3.417), 9.522 (s, 1H); ^{13}C NMR spectrum (DMSO-d_6): δ 56.524, 56.650, 110.385, 152.413, 162.805, and 178.667.

3. Results and discussion

3.1. Physical properties of solid catalysts

3.1.1. XRD patterns

Fig. 1 shows the XRD patterns of the different catalytic materials including n-DZ-05, DZ-05, SDZ-05, n-TZ-05, TZ-05 and STZ-05 samples. It is found that the distinct peaks of monoclinic zirconium oxide (m-) and tetragonal zirconium oxide (t-ZrO_2) both appear after being treated at 500 °C (DZ-05, TZ-05, SDZ-05 and STZ-05), in which the peaks at 2θ = 17.4°, 24.1°, 24.5°, 28.2° and 38.2° are assigned to the diffraction of (1 0 0), (0 1 1), (1 1 0) (−1 1 1) and (1 1 1) crystal of m-ZrO_2, and the peaks at 2θ = 30.3°, 35.3°, 50.4°, 50.7°, 60.3° and 74.5° are

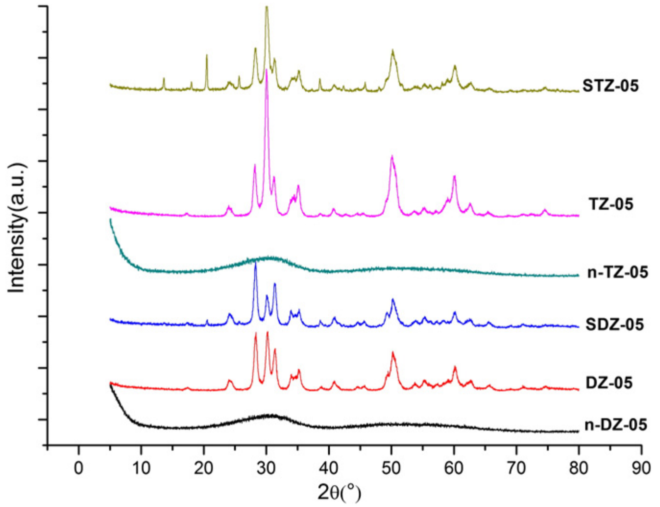

Fig. 1. XRD patterns of different catalytic materials.

attributed to the representative diffractions of t-ZrO_2. In addition, it can be seen that the content of m-ZrO_2 is higher in DZ-05 and SDZ-05 materials, while the content of t-ZrO_2 is higher in TZ-05 and STZ-05 material. Herein, the diffraction peak of SnO_2 is very weak which is probably contributed to the existence of nano oxide particles. In addition, there is no obvious effect on the diffraction peaks after sulfation with H_2SO_4. It confirms that the framework structure of SO_4^{2-}/SnO_2–ZrO_2 is always consistent with that of SnO_2–ZrO_2 material.

3.1.2. TG–DTG detection

The detection of TG–DTG of n-DZ-05 and SDZ-05 was performed and the results are shown in Fig. 2. As a result, it is found that there exist three obvious regions for the weight loss in which the scope of temperature are respectively 26–90 °C, 190–250 °C and 310–460 °C in the investigation of n-DZ-05 material. The first and second losses of weight are attributed to the removal of water absorbed in the surfaces of n-DZ-05. The third loss of weight is probably due to the dehydration of $Sn(OH)_x$ and $Zr(OH)_4$ to form the oxides. In the TG–DTG graphs of SDZ-05, the loss of weight appear in the regions of 45–90 °C, 170–225 °C and 550–780 °C, respectively. The first and second losses of weight are contributed to the removal of water absorbed in the surfaces of the catalysts. The third loss of weight is contributed to the removal of SO_x and the breakdown of acid structure. Otherwise, all the peaks showed that these processes were endothermic for the loss of weight. It should be motioned that TG–DTG results of n-TZ-05 and STZ-05 are similar with those of n-DZ-05 and SDZ-05 materials.

3.1.3. BET measurement

Textural properties of the Sn-based catalysts derived from the nitrogen physisorption are shown in Table 1. The results indicate that, compared to the n-DZ-05 and n-TZ-05, the surface area of SDZ-05 and STZ-05 are increased from 7.8 $m^2 \cdot g^{-1}$ to 259.9 $m^2 \cdot g^{-1}$ and from 12.6 $m^2 \cdot g^{-1}$ to 392.4 $m^2 \cdot g^{-1}$, respectively. Moreover, the whole pore volumes are also increased from 0.0409 to 0.467 $cm^3 \cdot g^{-1}$ (n-DZ-05 to SDZ-05) and from 0.107 to 0.663 $cm^3 \cdot g^{-1}$ (n-TZ-05 to STZ-05); otherwise, there is a certain decrease in the average pore diameter.

3.1.4. SEM images

In order to obtain the structure and morphology of different catalysts, the SEM characterizations are also performed. Fig. 3a–c shows the SEM images of n-DZ-05, DZ-05, and SDZ-05, and Fig. 3d–e indicates the SEM images of n-TZ-05, TZ-05 and STZ-05. As a result, it is found that there exists the loose surface in the prepared hydroxides n-DZ-05 and n-TZ-05, and the tight surfaces are formed in DZ-05 and TZ-05 which is the function of calcination at 550 °C. Moreover, the materials become more regular and smooth in the images of SDZ-05 and STZ-05. This should be the influence of immersion in H_2SO_4 solution.

3.1.5. TEM images

In the following, the catalytic materials are characterized by TEM technique. As shown in Fig. 4, the average particles are obtained after calcination at high temperature (Fig. 4b and e). The size of particles in sulfated samples is similar with the metal oxides (Fig. 4c and f), but the linkage between different particles become more popular which can be attributed to the effect on the aggregation of partial metal oxide particles in SDZ-05 and STZ-05 materials.

3.2. Catalytic activities of various catalysts in the dehydration of fructose

3.2.1. The catalytic performance of different Sn-based heterogeneous catalysts

In order to investigate the catalytic performance of different Sn-based catalysts, the dehydration of fructose is chosen as a model and the results are given in Table 2. First, it is found that the ratio of Sn and Zr has the influence on the catalytic activity of SnO_2–ZrO_2 catalyst. The yields of HMF are 45%, 54%, 51% and 34% when DZ-03, DZ-05, DZ-1 and DZ-2 are employed as the catalysts, respectively (entries 1–4). Moreover, the original n-DZ-05 has also quite a few catalytic activity, and the yield of HMF is 40% in the presence of n-DZ-05 in DMSO (entry 5). Furthermore, the sulfated SnO_2–ZrO_2 SDZ-05 showed higher activity for the fructose dehydration in which the yield of HMF arrives at 75% (entry 6). In the following, THF and THF–H_2O are used as solvents for the dehydration

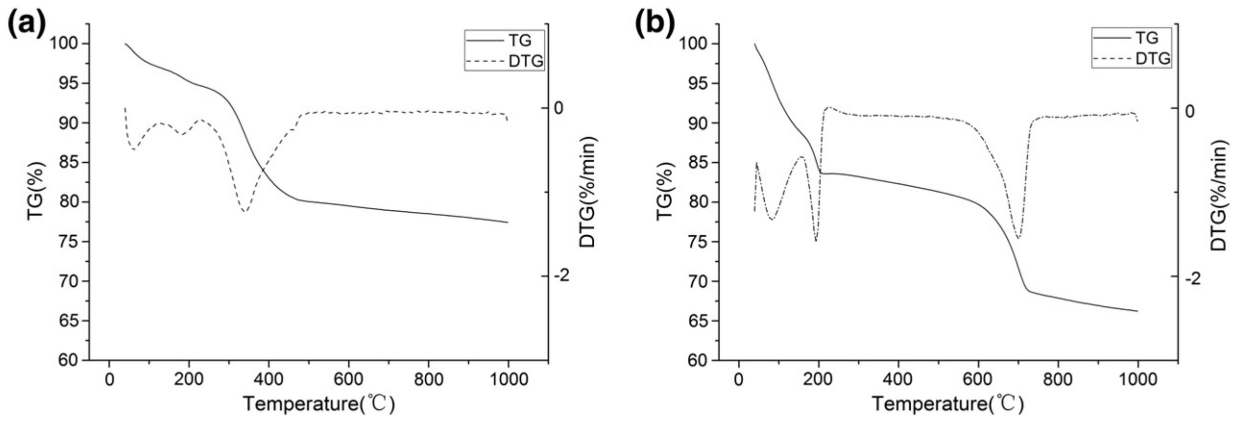

Fig. 2. The results for TG–DTG detection of n-DZ-05 catalyst (a) and SDZ-05 catalyst (b).

Table 1
The textural properties of different Sn-based heterogeneous catalysts.

Catalysts	BET surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})	Average pore diameter (nm)	
			BJH adsorption	BJH desorption
n-DZ-05	7.8	0.0409	7.52	21.8
n-TZ-05	12.6	0.107	4.74	21.7
SDZ-05	259.9	0.467	4.52	14.1
STZ-05	392.3	0.663	4.49	13.2

of fructose. It is found that 53% and 47% yields of HMF are obtained in THF–H_2O and THF when DZ-05 is used as the catalyst (entries 7 and 8). In addition, the yield of HMF is respectively 60% and 34% in the presence of SDZ-05 and n-DZ-05 in THF–H_2O solvent (entries 9 and 10). As comparison, the blank experiment is performed in absence of any catalyst, and only less than 1% yield of HMF is obtained (entry 11). On the other hand, the TZ-05, n-TZ-05 and STZ-05 are also used as the catalysts in the dehydration of fructose. As a result, 53%, 51% and 75% yield of HMF is obtained in DMSO (entries 12–14). This indicates that using $SnCl_4$ as the metal precursor of tin is superior to the Sn-based solid catalysts. On the other hand, the dehydration of glucose is investigated in the presence of DZ-05, TZ-05, SDZ-05 and STZ-05, in which 5%, 6%, 8%, 9% yields of HMF were obtained (entries 15–18). It shows that the conversion of ketose is superior to the conversion of aldose to HMF with these Sn-based heterogeneous catalysts.

Considering the above characterized physical properties, the catalytic activity of SDZ-05 is much higher than that of the n-DZ-05 which should be attributed to elevation of surface area (from 12.6 $m^2 \cdot g^{-1}$ to 259.9 $m^2 \cdot g^{-1}$) and pore volume (0.107 to 0.467 $cm^3 \cdot g^{-1}$) except the increase of acid sites in SDZ-05 compared to that in the n-DZ-05 catalyst (see IR spectra in SI). Besides, the more little average pore diameters of SDZ-05 and STZ-05 compared to those of n-DZ-05 and n-TZ-05 catalysts probably decrease the generation of polymeric by-products to improve HMF selectivity. In addition, the catalytic activities of TZ-05 and STZ-05 are higher than those of DZ-05 and SDZ-05, which is also correlated to the increase of surface area and pore volume of these materials. On the other hand, in DMSO solvent, the yield of HMF increases from 54% to 75% when the catalyst DZ-05 is replaced by SDZ-05; in THF–H_2O solvent, the yield of HMF only increases 7% (from 53% to 60%) when DZ-05 is changed to SDZ-05 catalyst. This is probably due to the excess water in the solution deactivating the active acid sites of SDZ-05 catalyst. It is also consistent with the SDZ-5 containing the numerous absorbed H_2O molecules, which can be concluded from the TG–DTG result of SDZ-05 catalyst.

3.2.2. The effect of reaction time

The effect of reaction time has been studied in order to reveal the character of catalytic reaction in the presence of $SO_4^{2-}/SnO_2–ZrO_2$ catalyst. Fig. 5 shows the results for the dehydration of fructose by SDZ-05 and STZ-05 catalysts during different periods. It is found that the yield of HMF gradually increases along with the time being increased from 30 min to 150 min. When the time was extended to 180 min or 210 min, the yield of HMF is decreased a little. It can be attributed that the occurrence of by-products is probably more rapid than the generation of HMF.

3.2.3. The effect of reaction temperature

The effect of temperature on the dehydration of fructose was also investigated with SDZ-05 and STZ-05 catalysts and the results are shown in Fig. 6. From these results, it is seen that the yield of HMF increases from 80 °C to 120 °C, and the yield began to decrease when the temperature was increased to 140 or 160 °C. Therefore, the optimum temperature is 120 °C in the dehydration reaction. For these SDZ-05 and STZ-05 catalysts, the tendency on the change of product yield kept in step which is due to their similar physical properties on crystal structure, average pore diameter and regular surface, etc.

3.2.4. The investigations on the recycle of catalysts

The recycles of DZ-05 and SDZ-05 have been examined in the dehydration of fructose. The investigations are performed at 120 °C for 2.5 h

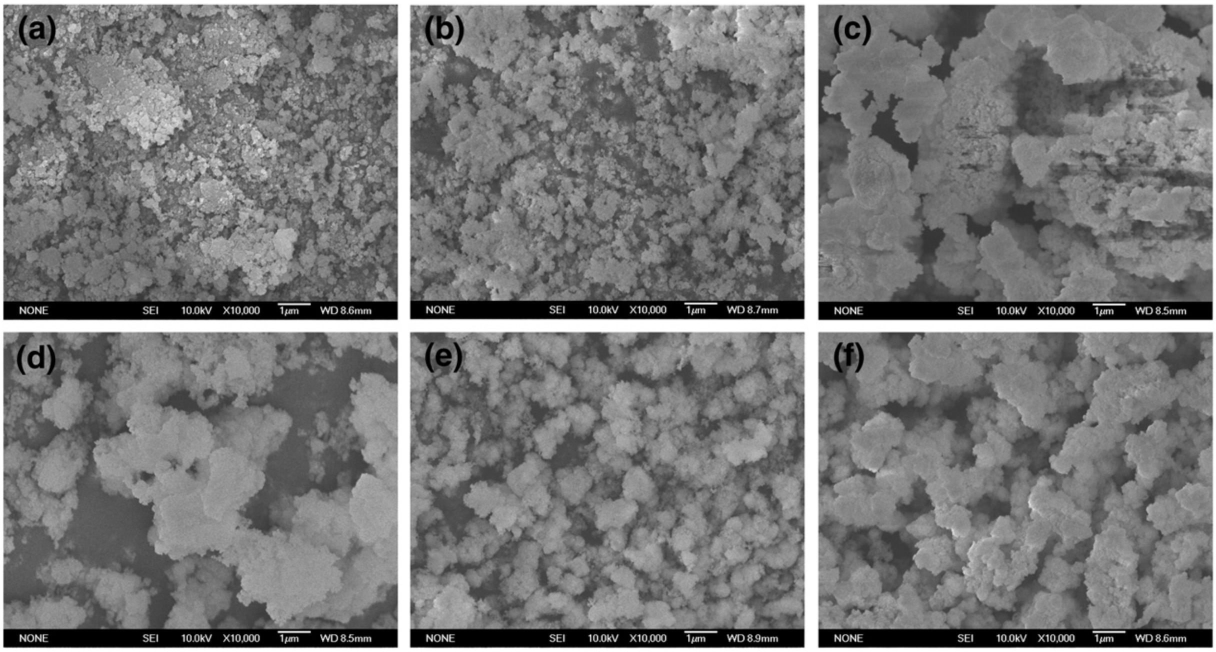

Fig. 3. The SEM images of different catalytic materials (a. n-DZ-05; b. DZ-05; c. SDZ-05; d. n-TZ-05; e. TZ-05; f. STZ-05).

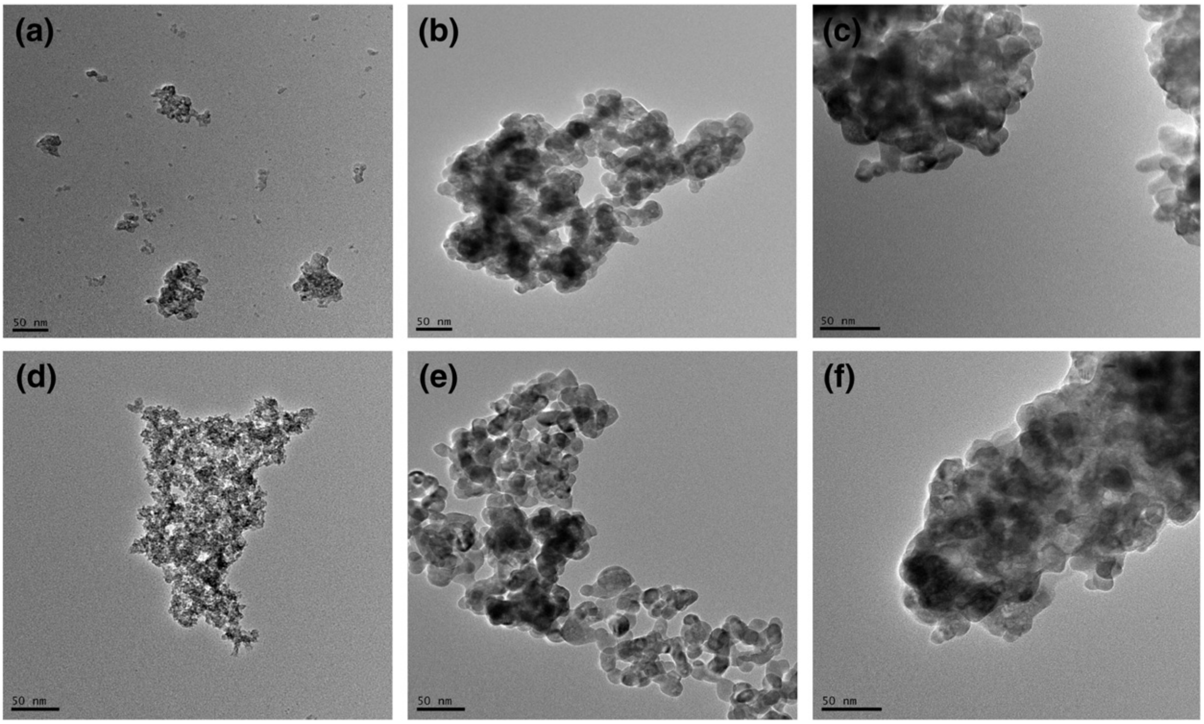

Fig. 4. The TEM images of different catalytic materials (a. n-DZ-05; b. DZ-05; c. SDZ-05; d. n-TZ-05; e. TZ-05; f. STZ-05).

in the presence of 20.0 wt.% catalyst. After the dehydration reaction, the catalyst was separated, and washed with anhydrous ethanol, and then dried at 80 °C for 12 h before being reused in the next run. As shown in Fig. 7, it can be seen that the yield of HMF is almost always about 72% unchanged in five recycle use of SDZ-05 catalyst. These experiment results show that the SDZ-05 catalyst is efficient and keeps stable in the dehydration of fructose. Combining the above TEM results, the regular and smooth surface of the catalyst should be responsible for the stability in the reaction.

4. Conclusions

In summary, the Sn-based solid acid SnO_2–ZrO_2 and SO_4^-/SnO_2–ZrO_2 were synthesized by combining the Sol–gel technique and impregnation method. The obtained catalytic materials were respectively characterized by XRD, TG, TEM, SEM and BET techniques. These catalysts have high thermal stabilities, regular crystal structures and moderate surface area. Furthermore, the efficient production of HMF from hexose is successfully performed with SO_4^-/SnO_2–ZrO_2 as the catalyst in DMSO and biphasic THF–H_2O system. The reaction temperature and time are further optimized. The recycle experiment shows that the SDZ-05 catalyst is still active after being used five times. So, these Sn-based solid catalysts are efficient for the conversion of fructose to HMF, which will be very useful for the biomass utilization in future.

Acknowledgment

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Table 2
Dehydration of fructose with different Sn-based solid catalysts.[a]

Entry	Substrate	Catalyst	Solvent	Yield of HMF (%)[b]
1	D-Fructose	DZ-03	DMSO	45
2	D-Fructose	DZ-05	DMSO	54
3	D-Fructose	DZ-1	DMSO	51
4	D-Fructose	DZ-2	DMSO	34
5	D-Fructose	n-DZ-05	DMSO	40
6	D-Fructose	SDZ-05	DMSO	75
7	D-Fructose	DZ-05	THF–H_2O	53
8	D-Fructose	DZ-05	THF	47
9	D-Fructose	SDZ-05	THF–H_2O	60
10	D-Fructose	n-DZ-05	THF–H_2O	34
11[c]	D-Fructose	none	THF–H_2O	<1
12	D-Fructose	TZ-05	DMSO	53
13	D-Fructose	n-TZ-05	DMSO	51
14	D-Fructose	STZ-05	DMSO	76
15	Glucose	DZ-05	DMSO	5
16	Glucose	TZ-05	DMSO	6
17	Glucose	SDZ-05	DMSO	8
18	Glucose	STZ-05	DMSO	9

[a] Reaction conditions: 1.0 g substrate, 0.2 g catalyst, in 10 mL solvent, for 2.5 h, at 120 °C.
[b] The results are obtained by HPLC analysis.
[c] The volume ratio of THF and H_2O is 3:1.

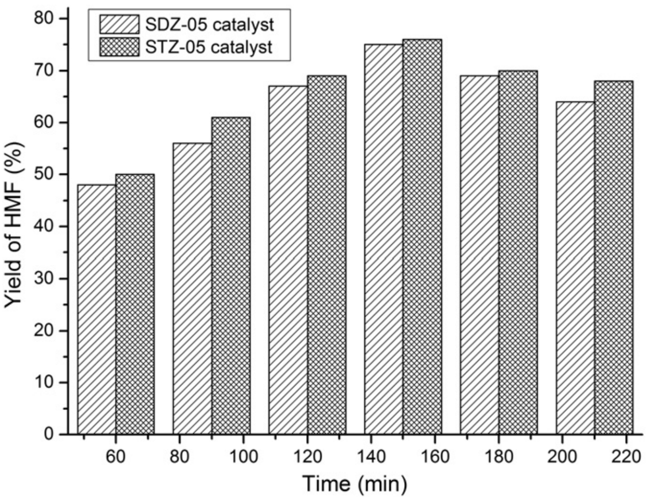

Fig. 5. The effect of reaction time with SO_4^{2-}/SnO_2–ZrO_2 in the dehydration of fructose (reaction conditions: 1.0 g substrate, 0.2 g catalyst, in 10 mL DMSO solvent, at 120 °C).

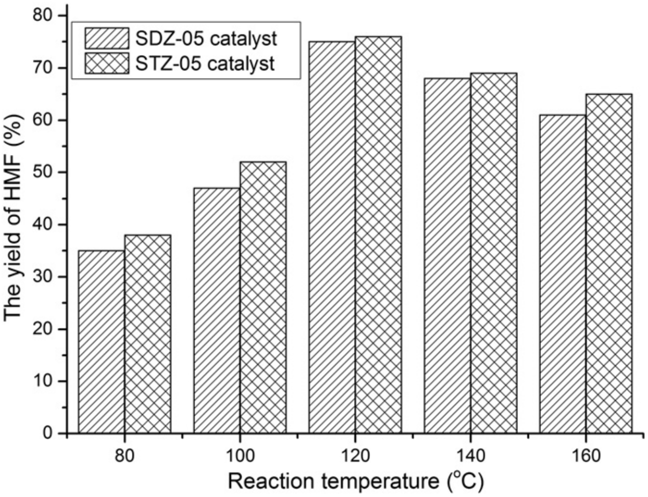

Fig. 6. The effect of reaction temperature on the dehydration of fructose (reaction conditions: 1.0 g fructose, 0.2 g catalyst, in 10 mL of DMSO, time 2.5 h).

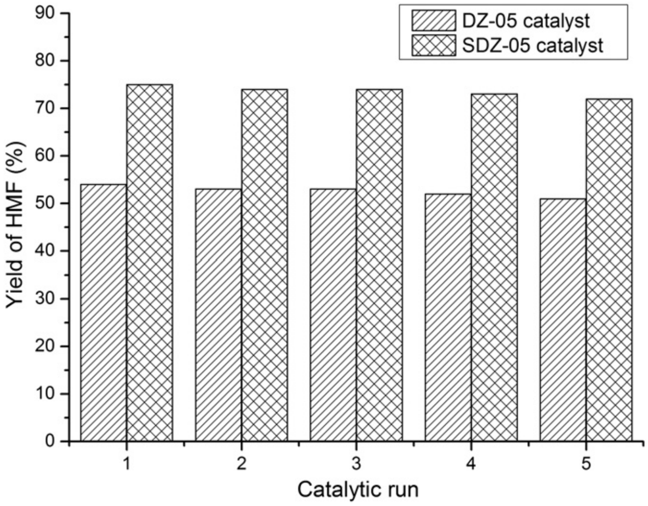

Fig. 7. The recycle experiment of DZ-05 and SDZ-05 catalysts (reaction conditions: 1.0 g fructose, 0.2 g catalyst, in 12 mL of DMSO, time 2.5 h).

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Appendix A. Supplementary data

The IR spectra, partial TG–DTG results of catalysts and the GC/MS spectra, NMR spectra of HMF are contained in the supporting information. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.catcom.2014.02.023.

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