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Article

One-pot cascade conversion of xylose to furfuryl alcohol over a bifunctional Cu/SBA-15-SO₃H catalyst

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ABSTRACT

The conversion of hemicellulose-derived xylose to furfuryl alcohol is a practical procedure for producing value-added chemicals from biomass. In this study, a bifunctional Cu/SBA-15-SO₃H catalyst was employed for the one-pot catalytic conversion of xylose to furfuryl alcohol with a yield of up to 62.6% at the optimized conditions of 140 °C, 4 MPa, and for 6 h in a biphasic water/*n*-butanol solvent. A high reaction temperature resulted in further hydrogenation to 2-methyl furan, while a high hydrogen pressure led to a side hydrogenation reaction to xylitol. The biphasic solvent allowed xylose solvation as well as furfuryl product extraction. The acidic –SO₃H sites and Cu sites co-existed, maintained a balance, and cooperatively catalyzed the cascade conversion. Excessive acidic sites and large pores could promote the xylose conversion, although a low furfuryl alcohol yield was obtained. This catalytic system could be potentially applied to the one-pot synthesis of furfuryl alcohol from hemicellulose-derived xylose.

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1. Introduction

The adequate utilization of non-edible lignocellulosic biomass is paramount for sustainable economic development [1–3]. Hemicellulose, one of the three major components of biomass, consisting of mainly pentoses and remnant hexoses, can be hydrolyzed to monosaccharide products, such as xylose [4–6]. Xylose can be converted to various high-value green chemicals, such as furfural derivatives, including furfuryl alcohol, 2-methyl furan, and tetrahydrofurfuryl alcohol, which find potential applications as green solvents, biofuels, and synthetic building blocks [7,8]. Among them, furfuryl alcohol, an essential

industrial chemical, has been widely used in the manufacture of chemically stable resins, fibers, and essential medicine, as well as the production of levulinic acid [9,10].

At present, the industrial production of furfural alcohol from biomass is carried out via two separate processes. Biomass containing hemicellulose was initially hydrolyzed and dehydrated in homogeneous mineral acid to produce furfural [11]; subsequently, furfural was hydrogenated into the target product, furfuryl alcohol, over a copper chromate heterogeneous catalyst [12]. These processes always require a furfural production factory and hydrogenation equipment. Meanwhile, these two sections suffer from environmental and safety haz-

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ards owing to the acidic effluent and instrument-corrosion problems introduced by inorganic acids, followed by the toxicity of chromate [8,9,12]. To address these shortcomings, the application of catalytic systems to each individual step has been explored separately, and great achievements have been recorded. The reported solid acid replacements of inorganic acids such as resins, functionalized C/Si materials, and metal oxides have an intensive capacity for the conversion of xylose to achieve increased furfural yields [13–15]. As for the researches on alternatives to copper chromate, intensive efforts were devoted to supported Cu catalysts due to their preferential hydrogenation of C=O bonds [10,12]. The synergistic effect of the coexisting Cu⁰ and Cu⁺ species in Cu-based catalysts is the key for excellent performance in the furfural hydrogenation reaction to furfural alcohol, in which Cu⁰ promotes hydrogen decomposition, while Cu⁺ sites activate acyl groups [16].

Recently, the one-pot conversion of hemicellulose-derived xylose to furfuryl alcohol, without intermediate separation, has attracted increasing attention [17–20]. Most studies on the one-pot synthesis of furfuryl alcohol from xylose concentrate on the usage of a dual catalytic system consisting of a physical mixture of solid acid and metallic hydrogenation catalyst in one reactor, in which acid and metal sites were located independently on different surfaces [18,20]. For instance, Perez et al. [19] used dual catalysts composed of sulfated ZrO₂ physically mixed Pt/SiO₂ as acid and metal sites to convert xylose in a H₂O/2-propanol biphasic solvent at 150 °C, affording 24% yield of furfuryl alcohol and 21% of furfural. These one-pot cascade syntheses suffer from various simultaneous competitive reactions in one-pot synthesis [6,21]. As shown in Scheme 1, xylose and its isomerization product, xylulose, can be directly hydrogenated to xylitol on metal sites, or converted into glyceraldehyde and glycolaldehyde via retro-aldol condensation, and ultimately reduced to glycerol and ethylene glycol [22]. Meanwhile, the target product, furfuryl alcohol, may also continue to undergo side reactions, yielding levulinic acid and 2-methyl furan on the acid and metal sites, respectively [21]. The coking process via the condensation of xylose and/or furfural derivatives also reduces the carbon efficiency [6,21].

The diversity and complexity of the pathway for the one-pot conversion of xylose make it a challenge to balance the active sites in the catalytic system to maximize the yield of furfuryl alcohol. The application of bifunctional catalysts with both acid and metal sites on the same support is an effective approach to

improve this multistep strategy [23,24]. Fraga group [25] synthesized various acid-functionalized carbon nanotubes-supported noble metal catalysts to convert xylose, and Ru exhibited the most active performance (Ru > Pd > Pt > Rh ~ Au), providing 84% yield of xylitol and 9% yield of furfuryl alcohol. However, to the best of our knowledge, the studies on the one-pot conversion of xylose to furfuryl alcohol over bifunctional catalysts are centered on precious metals, which have a high cost.

According to the performance of the traditional CuCr catalyst [6] as well as our previous work [26], Cu could be suitable for catalyzing the furfural hydrogenation step. Meanwhile, based on our previous work [27,28], SBA-15, which has a tunable mesoporous framework structure and can be functionalized by sulfonic acid, could be an appropriate acidic support for xylose dehydration. Therefore, in this work, sulfonic acid functionalized SBA-15-supported Cu catalyst was employed for the one-pot conversion of xylose to furfuryl alcohol. The availability of anchoring acid and metal sites, as well as the physico-chemical properties of the catalysts were examined by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), Fouriertransform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), inductively coupled plasma optical emission spectrometry (ICP-OES), X-ray fluorescence (XRF), NH₃-temperature-programmed desorption (NH₃-TPD) and N₂ physico-adsorption characterizations. The following reaction conditions were optimized: reaction temperature, hydrogen pressure, reaction time, and solvent system. The impact of the ratio of acid and metal sites, as well as the size of mesopore on the furfuryl alcohol production was also studied.

2. Experimental

2.1. Catalyst preparation

A series of sulfonic acid functionalized SBA-15 carriers was synthesized by the co-condensation method. Template (P123), silicon source (tetraethyl orthosilicate, TEOS), and sulfur source ((3-mercaptopropyl) trimethoxysilane, MPTMS) were co-crystallized. Thereafter, the supported sulfhydryl group was oxidized to sulfonic group by hydrogen peroxide. Cu was then impregnated and reduced by NaBH₄. The simplified material synthesis process is shown in Scheme 2. Cu/SBA-15 was obtained by the same impregnation process described in a refer-

Scheme 1. Possible reaction routes of the one-pot transformation of xylose to furfuryl alcohol.

Scheme 2. Simplified process of the catalyst synthesis.

ence, including the impregnation of Cu on bare SBA-15 synthesized by the above-described co-condensation method without adding MPTMS and hydrogen peroxide. A detailed synthesis procedure is described in Supporting Information.

2.2. Catalyst characterization

Nitrogen adsorption-desorption experiments were performed on the Micromeritics ASAP 2020 analyzer at 77 K, and the BET and BJH methods were used to calculate the specific surface area and pore size distribution of catalysts from the adsorption-desorption curves, respectively. Inductively coupled plasma optical emission spectrometer (ICP-OES, Varian Vista-MPX) was used to analyze the Cu and Ru contents of samples. The peaks at 327.393 nm and 339.9 nm were used respectively as the Cu or Ru characteristic wave lengths to identify the Cu^{2+} and Ru^{3+} concentration of samples. The powder X-ray diffraction (XRD) patterns of samples were obtained on the PANalytical X'pert diffractometer equipped with a graphite-filtered $\text{Cu } K\alpha$ radiation operated at 45 kV and 200 mV. The scanning of diffraction angle ranges from 10 degree to 90 degree with a step of 0.01 degree. The transmission electron microscopy (TEM) images as well as the high-resolution transmission electron microscope (HRTEM) pictures of catalysts were obtained from a JEOL-2010 electron microscope. Prior to the experiment, the ethanol suspension of the sample was dispersed by ultrasonic wave treatment and deposited on a substrate sheet containing free copper. EDS analysis was done on JEOL X-Ray micro-analysis system TEM 200. Scanning electron microscopy (SEM) microphotographs and EDX-elemental mapping were obtained using a GeminiSEM 500

electron microscope. Fourier transform infrared spectroscopy (FT-IR) from 4000 to 400 cm^{-1} was obtained on a Nicolet 8700 Thermo Scientific FT-IR spectrometer with a resolution of 0.4 cm^{-1} to detect the presence of sulfonic acid groups in the silica structural framework. X-ray fluorescence spectrometry (XRF) was performed on a Shimadzu XRF-1800 spectrometer to determine the S content of materials. The acidity was investigated by NH_3 -temperature-programmed desorption (NH_3 -TPD) using the home-built adsorption instrument coupled with a gas chromatograph. Before the test, 60 mg of the sample was pre-treated at 150 $^{\circ}\text{C}$ for 2 h under an Ar purge, and then subjected to adsorption of NH_3 and Ar mixed steam of at 80–350 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. The desorbed NH_3 was absorbed by 0.005 mol/L dilute sulfuric acid aqueous solution, which was then conducted reverse-titration with 0.01 mol/L NaOH solution for three times to quantify an average value of the acidity representing the total acid sites in the unit of mmol/g. The acid density is calculated by acidity on catalyst per specific surface area in the unit of mmol/ m^2 . Thermogravimetric analysis (TGA) was used to verify the thermal stability of the sulfonic acid groups on materials and conducted on a Perkin Elmer TL-9000 device. Samples were heated from 25 $^{\circ}\text{C}$ to 1000 $^{\circ}\text{C}$ in a flowing nitrogen atmosphere at a slope of 10 $^{\circ}\text{C}/\text{min}$.

3. Results and discussion

3.1. Catalyst characterization results

The structures of SBA-15 and sulfonated SBA-15 were assessed by the low-angle range of the XRD patterns shown in Fig. 1A. The XRD pattern of SBA-15 showed a strong diffraction peak at 0.9 $^{\circ}$, reflecting the formation of the (100) facet of SBA-15. Meanwhile, two relatively small diffraction peaks were observed at 1.5 $^{\circ}$ and 1.7 $^{\circ}$, corresponding to the (110) and (200) facets of SBA-15, respectively, which confirmed that the SBA-15 materials with well-ordered mesoporous structures were successfully synthesized [29,30]. Although the high-order (110) and (200) diffraction peaks on sulfonated SBA-15 and Cu/SBA-15 were hardly distinguishable, the signal of the (100) facet revealed that the mesoporous structure of SBA-15 was maintained with a slight decrease in crystallinity [31].

The wide-angle range of XRD tests, shown in Fig. 1B, was

Fig. 1. (A) The low-angle range and (B) wide-angle range of the XRD patterns of the parent SBA-15 and supporting materials.

Fig. 2. TEM images of (A) SBA-15 and (B) SBA-15-SO₃H. (C) Cu/SBA-15-SO₃H. (D) SEM image and EDX element maps of Cu, S, and Si of Cu/SBA-15-SO₃H and (E) the HRTEM image.

performed to distinguish the actual metal species on the bulk Cu-based catalysts. The broad diffraction peak at around 23°, registered in all maps, corresponded to the Si-based support [32]. Except it, both Cu-based catalysts exhibited distinct characteristic diffraction peaks located at about 43.1° and 50.5°, attributed to the (111) plane of metallic Cu (copper, PDF No 70-3039) [33], accompanied by several characteristic peaks related to the Cu₂O phase indexed in Cuprite, Pdf: 77-0199 [34]. Briefly, Cu⁰ and Cu⁺ species coexisted on Cu/SBA-15 and Cu/SBA-15-SO₃H.

The microscopic morphology of the SBA-15 materials was observed in electron microscopic images (Fig. 2). The TEM picture of SBA-15, shown in Fig. 2A, exhibited the formation of a regular mesoporous structure [29,31]. Although setting together the Cu and -SO₃H groups on SBA-15 introduced some amorphous organization, which can be inferred from the blurry details in Figs. 2B and 2C, the mesoporous framework was integrally retained. The microstructure in the SEM picture of the grafted SBA-15 material shown in Fig. 2D is similar to that of the parent SBA-15 material [23,35]. The morphology was in consonance with the conclusion drawn by XRD patterns.

The HRTEM images of the SBA-15 material grafted with both metal and acid sites are shown in Fig. 2E. The clear lattice fringes were obtained as 0.244 and 0.209 nm, corresponding to the (111) plane spacings of Cu₂O and metallic Cu, respectively [33,36]. The distributions of Cu and S are presented in SEM-EDX elemental mapping, which reveal that the -SO₃H groups were uniformly dispersed through the carrier [37], profiting from the co-condensation method with the S-containing organosilanes, while Cu displayed a small bulk

aggregation, owing to the in-situ chemical reduction of the metal.

The XPS spectra were used to analyze the metal species on the surfaces of Cu/SBA-15 and Cu/SBA-15-SO₃H. The Cu 2p spectra of Cu/SBA-15-SO₃H, shown in Fig. 3A, displayed only a sharp characteristic peak at 933 eV, corresponding to the Cu⁺ species or Cu⁰, while a few surface-oxidized Cu²⁺ species on Cu/SBA-15 was confirmed by the appearance of the characteristic peak at 935.3 eV and broad satellite peak at around 945 eV [12]. The deconvolution of the Cu LMM Auger spectra shown in Fig. 3B was recorded to distinguish the Cu⁺ species from Cu⁰, where both Cu-based catalysts demonstrated three symmetrical overlapping peaks. Among them, the peaks occurring at ca. 918.2 and 916.3 eV were ascribed to Cu⁰ and Cu⁺ species, respectively [12]. This detection was in consonance with the bulk speculation from the XRD pattern, confirming that the Cu₂O phase and metallic Cu coexisted on Cu/SBA-15 and Cu/SBA-15-SO₃H.

The grafted -SO₃H groups in the SBA-15 structure were further analyzed by FT-IR. The spectra of both the parent SBA-15 and sulfonated SBA-15, shown in Fig. 4, exhibit two relative intensive bands at 1090 and 3400 cm⁻¹, belonging to the asymmetric Si-O-Si and O-H vibrations, respectively. Meanwhile, the same typical silica characteristic peaks of symmetric stretching vibrations from the Si-O bonds at 800 cm⁻¹ and bending vibrations from the Si-O-Si bonds at 466 cm⁻¹ were observed on both the SBA-15 and SBA-15-SO₃H spectra, as previously reported in the literature [30,31]. Besides, the peaks at 965 and 1620 cm⁻¹ were associated with the Si-O-H bonds and bending vibrations from O-H bonds, respec-

Fig. 3. (a) XPS spectra in the Cu 2p region and (b) Cu LMM XAES spectra of Cu/SBA-15 and Cu/SBA-15-SO₃H.

Fig. 4. FT-IR profiles of SBA-15 and SBA-15-SO₃H.

Fig. 5. TGA and DTG profiles of SBA-15-SO₃H.

tively [38]. Distinctive features appearing on sulfonated SBA-15 was detected by the special bands at 1180 and 690 cm⁻¹, assigned to the stretching vibrations of the S=O and S-O bonds. This corroborated the availability of the -SO₃H groups on the functionalized SBA-15 material, which ascertained the crucial acidity of the catalyst [30,35,38]. The peaks at 2850 and 600 cm⁻¹ corresponding to the stretching vibrations of the C-H and C-S bonds, stemmed from the residual S-containing organosilanes (MPTMS) for the incorporation of SO₃H [38,39]. The presence of a weak S-H vibration signal at 2400 cm⁻¹ unveiled the minute quantity of non-oxidized sulphydryl functionality remnant [30,31].

Table 1

Physical and chemical properties of materials.

Material	S ^b (mmol/g)	Cu ^c (wt%)	S _{BET} (m ² /g)	Pore size ^d (nm)	Pore volume ^e (cm ³ /g)	Acidity ^f (mmol/g)	Acid density ^g (mmol/m ²)
SBA-15	—	—	748.4	6.1	1.08	0.02	0.0000
SBA-15-SO ₃ H	1.47	—	595.7	5.0	0.64	1.36	0.0023
Cu/SBA-15-SO ₃ H	1.12	18.3	433.2	4.1	0.56	0.98	0.0023
SBA-15-SO ₃ H(HI) ^a	0.20	—	695.4	5.7	0.95	0.19	0.0003

^a Prepared by the hydrothermal impregnation method. ^b Determined by XRF. ^c Determined by ICP-OES. ^d BJH desorption average pore diameter (4V/A). ^e BJH desorption cumulative volume of the pores between 17.0 Å and 3000.0 Å diameter. ^f Determined by NH₃-TPD. ^g Calculated by the ratio of acidity/S_{BET}.

The thermostability of the acid sites originating from successful functionalization of the -SO₃H groups into SBA-15 was evaluated by TGA characterization. The TGA curve shown in Fig. 5 exhibited three distinct desorption peaks. The 6.9% mass loss peak below 130 °C was associated with the desorption of the physically adsorbed water on the hydrophilic -OH groups [23,40]. The other two peaks indicating a total of 18.8% mass loss between 290 and 650 °C were attributed to the successive thermal decomposition of incorporated organic sulfonic acid groups [23,40]. The mass loss in this stage is attached to the valuable information that the incorporation content of the propyl-sulfonic acid groups was 1.53 mmol/g during the synthesis step, which is almost in line with the quantitative assay of S determined by XRF. According to the above thermotolerance analysis, NaBH₄ was selected for the in situ chemical reduction of the metal sites on the catalyst to ensure the complete survival of acid sites. A simplified pictorial process of the surface assembly of single multifunctional catalysts is shown in Scheme 2.

The actual metal loadings on the single bifunctional catalysts were determined by ICP analysis, and the result, shown in Table 1, reveals that the content of Cu was 18.3 wt%. The S content on sulfonated SBA-15 was 1.47 mmol/g by XRF measurement, indicating that a loss of about 21% was incurred after metal loading. The porosity properties shown in Table 1 describe the high specific surface area of the parent SBA-15 as 748.4 m²/g, along with a mean pore size of 6.1 nm [29]. The porous characteristics including the specific surface area, pore size as well as the pore volume were significantly decreased in the modified SBA-15, while the ordered mesoporous structures were maintained over all the catalysts, as verified by the TEM pictures [23,30,32]. The acidity of the various materials shown in Table 1 was determined by NH₃-TPD profiles. The detailed quantifying description is included in Supporting Information. The incorporation of sulfonic acid groups into SBA-15 enhanced the acidity from 0.02 to 1.36 mmol/g, while the loading of metal sites decreased the acidity to 0.98 mmol/g. All the above progressive decreasing tendencies, as expected, suggested the valid anchoring of acid and metal sites on different the surface sites of SBA-15 [23]. In addition, a hydrothermal impregnation method in concentrated sulfuric acid for the synthesis of sulfonated mesoporous silica was employed as a control, and the obtained SBA-15-SO₃H(HI) material is characterized in Table 1. The preservation of the ordered porous structure could be corroborated by the relatively high BET data and large mesoporous pore volume compared with single bi-

Table 2Performance of various materials on the conversion of xylose in one-pot at 130 °C and 3 MPa H₂.

Entry	Catalyst	Conv. ^a (%)	Selectivity (%)						C ^b (%)
			Xylitol	Furfural	Furfuryl alcohol	Xylulose	2-methyl furan	Levulinic acid	
1	Cu/SBA-15-SO ₃ H	93.7	6.6	10.4	63.4	10.8	0	0	91.7
2	SBA-15	4.9	0	0	0	0.3	0	0	95.2
3	SBA-15-SO ₃ H	97.3	2.5	70.1	1.1	12.8	0	3.5	90.3
4	Cu/SBA-15	52.8	92.2	0	0	1.4	0	0	96.5
5	SBA-15-SO ₃ H physical mixed Cu/SBA-15	95.6	14.9	23.5	38.1	11.1	1.0	2.7	91.7
6	SBA-15-SO ₃ H(HI) ^c	10.4	3.2	46.7	1.9	4.8	0	0.2	95.4

^a Conversion of xylose under conditions of 0.83 mmol xylose, 10 mL of water-*n*-butanol (1/3 volume ratio), 100 mg of the catalyst, and 6 h. ^b Carbon balance (the calculation formula is shown in Supplementary Information). ^c Prepared by the hydrothermal impregnation method.

functional catalysts, while the content of the functionalized S in company with the acidity on SBA-15 was extremely low.

3.2. Catalytic reactions

The parent SBA-15 material and a series of sulfonic acid functionalized SBA-15 supported materials were evaluated by the one-pot transformation of xylose to furfuryl alcohol in a bi-phase solvent consisting of water and *n*-butanol at 130 °C and 3 MPa H₂. The catalysts containing metal sites were chemically pre-reduced by NaBH₄, and subsequently introduced into the liquid phase reaction. As exhibited in Table 2, 93.7% xylose conversion and 63.4% selectivity of furfuryl alcohol were achieved over the Cu-SBA-15-SO₃H catalyst in 6 h. The Ru-based catalyst led to over-hydrogenation to 2-methyl furan, as shown in Table S2.

As shown in Table 2, entry 2, only 4.9% xylose conversion was achieved on the parent SBA-15 material with xylulose being the only product. To reveal the respective essential roles of acid sites and metal sites on the single bifunctional catalyst, two control experiments were performed on SBA-15 with only independent acid sites or metal sites (SBA-15-SO₃H and Cu/SBA-15), and the performance is shown in entries 3 and 4. The conversion of xylose reached 97.3% over the SBA-15-SO₃H catalyst, and the main product was furfural via dehydration over the acid sites, while xylose reached only 52.8% conversion over Cu/SBA-15, and the main product was xylitol with 92.2% selectivity. This proved that the acid sites significantly enhanced the catalytic activity and the xylose dehydration to furfural, as well as inhibited the side reactions of the xylose hydrogenation; subsequently, the cooperative metal sites continued to hydrogenate the intermediate furfural to the target product, furfuryl alcohol, and protected furfuryl alcohol from the hydrolysis reaction on the acid sites to inhibit the formation of the by-product, levulinic acid.

Both acid and metal sites were indispensable for the one-pot conversion of xylose to furfuryl alcohol; therefore, the dual catalytic system consisting of a physical mixture of SBA-15-SO₃H and Cu/SBA-15 was used for comparison. As shown in entry 5, the product distribution on the dual catalytic system was highly different from that on the bifunctional catalyst (entry 1), in which the selectivity of various by-products significantly increased. This indicates that, as previously discussed [23,24], various intermediate products underwent ran-

dom reactions on random catalytic sites, resulting in the low selectivity toward furfuryl alcohol, as only 38.1% was afforded. Namely, the product was more evenly distributed on the dual catalytic system since the acid and metal sites resided on different surfaces, while the bifunctional catalyst with both finely dispersed acid and metal sites setting together on the same surface could aid the reaction to proceed orderly along the target route to obtain furfuryl alcohol with high selectivity.

In addition, the performance of the sulfonated mesoporous silica obtained from a hydrothermal impregnation method in concentrated sulfuric acid is shown in entry 6, indicating an extremely poor catalytic activity of SBA-15-SO₃H(HI), with only 10.4% xylose conversion, compared with that of SBA-15-SO₃H prepared by the co-condensation method. The lower content of S and acidity on SBA-15-SO₃H(HI), represented in Table 1, were responsible for its relatively weak performance, demonstrating that the hydrothermal impregnation applied to the functional sulfonic acid groups on SBA-15 did not work well.

It had been verified from Table 2 above that the co-existing bifunctional acid-metal sites were more favorable for the direct production of furfuryl alcohol in the one-pot synthesis to avoid the formation of by-products. To further investigate the impact of acid and metal sites, catalysts with varying S contents were synthesized by adjusting the ratio of the Si source to the S source (TEOS/MPTMS).

The chemical composition and properties, as well as the catalytic performance of Cu/SBA-15-SO₃H with different loadings of the -SO₃H groups, are summarized in Table 3. With the decrease in the molar ratio of TEOS/MPTMS from 10 to 3.5, the content of S and the total acid sites increased gradually. Meanwhile, the conversion of xylose increased with increasing acidity and reached the maximum at 95.1% over Cu/SBA-15-SO₃H(3.5). However, the selectivity of furfuryl alcohol was the highest (63.4%) at a different TEOS/MPTMS ratio of 5.

To further study how the acid/metal ratio affected the distribution of the by-products, time-dependent curves of the product distribution and xylose conversion were collected at 140 °C on the catalysts with varying acidities, and are shown in Fig. 6. Within the same reaction time, the xylose conversion and the selectivity of the isomerization product, xylulose, were significantly increased with the enhanced acidity on the catalyst, indicating the promoting effect of the acid sites on the catalytic activity and xylose isomerization. The time-correlated curves of

Table 3Chemical properties of Cu/SBA-15-SO₃H with different contents of acid sites and performance in the one-pot conversion of xylose.

Material	TEOS/MPTMS molar ratio	S ^a (mmol/g)	Cu ^b (wt%)	Acidity ^c (mmol/g)	Acid/Metal molar ratio ^d	Conv. (%) ^e	Sel. FFA (%)	C (%)
Cu/SBA-15-SO ₃ H(10)	10	0.75	18.6	0.59	0.26	87.4	56.9	93.1
Cu/SBA-15-SO ₃ H(5)	5	1.12	18.3	0.98	0.40	93.7	63.4	91.7
Cu/SBA-15-SO ₃ H(3.5)	3.5	1.33	17.2	1.25	0.49	95.1	48.7	89.2

^a Determined by XRF. ^b Determined by ICP-OES. ^c Determined by NH₃-TPD. ^d Based on acid sites, as estimated by the S content. ^e Conversion of xylose under the conditions of 0.83 mmol xylose, 10 mL water-*n*-butanol (1/3 volume ratio), 100 mg of the catalyst, 130 °C, 3 MPa H₂, and 6 h.

Fig. 6. Product evolution of the conversion xylose in the one-pot synthesis over (A) Cu/SBA-15-SO₃H(10), (B) Cu/SBA-15-SO₃H(5), and (C) Cu/SBA-15-SO₃H(3.5). Reaction conditions: 0.83 mmol xylose, 10 mL of water-*n*-butanol (1/3 volume ratio), 100 mg of the catalyst, 140 °C, 3 MPa H₂.

the xylulose yield over all the catalysts exhibited rapid accumulation and dominated the product distribution at the initial stage of the reaction, followed by gradual consumption as the reaction proceeded, in line with previous reports [41]. The selectivity of furfural was less than 12% over any bifunctional catalysts, and was consistently lower than that in the dual catalytic system, as shown in entry 5, Table 2. Meanwhile, furfuryl alcohol was the main product.

The selectivity of the hydrogenated products, xylitol and 2-methyl furan, gradually decreased as the acidity of the catalysts increased, and the hydrolyzation product, levulinic acid, formed on the acid sites appeared over Cu/SBA-15-SO₃H(3.5), which had the highest amount of acid sites, resulting in the simultaneously reduced selectivity of furfuryl alcohol. This revealed that the excessive metal sites on Cu/SBA-15-SO₃H with a relatively low amount of acid sites would lead to the direct hydrogenation of xylose and over-hydrogenation of furfuryl alcohol. In contrast, the excessive acid sites on Cu/SBA-15-SO₃H(3.5) with the highest amount of acid sites contributed to the hydrolysis of furfuryl alcohol. Therefore, maintaining a balanced ratio between the acid and metal sites would promote the conversion of xylose into furfuryl alcohol and inhibit the occurrence of competitive reactions. Herein, Cu/SBA-15-SO₃H(5) with the mole ratio of acid and metal sites

as 0.4 afforded the highest selectivity of furfuryl alcohol. Therefore, in this study, the molar ratio of TEOS/MPTMS for synthesizing the Cu/SBA-15-SO₃H catalyst was maintained as 5 unless otherwise specified.

3.3. Inhibition of condensation by pore diameter

Arias group [42] had employed sulfonic acid functionalized SBA-15 catalysts with controlled pore properties to realize the highest selectivity of furfural (85%) at 96% xylose conversion. To further investigate the effect of the pore size of the carrier on the conversion of xylose to furfuryl alcohol, Cu-SBA-15-SO₃H catalysts with varying pore sizes were synthesized. The pore properties were determined by nitrogen physic-adsorption, as shown in Fig. S2. The pore size distribution of the common Cu/SBA-15-SO₃H catalyst was the narrowest (about 4 nm), while those of Cu/SBA-15-SO₃H-D7 and Cu/SBA-15-SO₃H-D12 were about 7 and 12 nm, respectively. The performances of these three catalysts for the one-pot conversion of xylose to furfuryl alcohol are shown in Table 4.

Increasing the average pore size from 4 to 12 nm slightly improved the xylose conversion from 93.7% to 95.1% and significantly triggered the competitive reactions, including increasing the xylitol selectivity from 6.6% to 11.6% and the

Table 4Performance of the catalysts with varying mean pore sizes in the conversion of xylose in the one-pot synthesis at 130 °C and 3 MPa H₂.

Catalyst	Cu (wt%)	Acid/metal molar ratio	Mean pore size (nm)	Conv. ^a (%)	Selectivity (%)						C ^b (%)
					Xylitol	Furfural	Furfuryl alcohol	Xylulose	2-Methyl furan	Levulinic acid	
Cu/SBA-15-SO ₃ H	18.3	0.40	4	93.7	6.6	10.4	63.4	10.8	0	0	91.7
Cu/SBA-15-SO ₃ H-D7	17.9	0.39	7	94.8	9.7	10.1	50.5	12.0	0	1.3	84.3
Cu/SBA-15-SO ₃ H-D12	18.4	0.40	12	95.1	11.6	9.9	42.6	11.4	0	3.8	77.0

^a Conversion of xylose under the conditions of 0.83 mmol xylose, 10 mL of water-*n*-butanol (1/3 volume ratio), 100 mg of the catalyst, and 6 h.

Fig. 7. Effect of the reaction temperature on the one-pot conversion of xylose over Cu/SBA-15-SO₃H. Reaction conditions: 0.83 mmol xylose, 10 mL of water-*n*-butanol (1/3 volume ratio), 100 mg of the catalyst, 3 MPa H₂, 6 h.

progressive increase in the selectivity of levulinic acid. These side reactions led to a severe decrease in the selectivity of furfuryl alcohol from 63.4% to 42.6%. The selectivity of both furfural and xylulose exhibited a downward trend as the pore size increased, together with a relatively sudden loss of the total carbon balance. Meanwhile, the relatively deep color of the liquid mixture after the reaction, as shown in Fig. S3, was observed with the increasing pore size. These phenomena proved that the increase in the pore size promoted the formation of humins, which could be explained by the failure of the shape selectivity owing to the extremely large zeolite structures.

3.4. Effect of reaction conditions

The effect of the reaction temperature on the performance of the Cu/SBA-15-SO₃H catalyst in the one-pot conversion of xylose was explored. As shown in Fig. 7, the conversion of xylose was significantly enhanced with the increase in temperature and reached a maximum of 99% over Cu/SBA-15-SO₃H at

Fig. 8. Effect of pressure on the one-pot conversion of xylose over Cu/SBA-15-SO₃H at 140 °C. Reaction conditions: 0.83 mmol xylose, 10 mL of the solvent, 140 mg of the catalyst, 6 h.

Fig. 9. Effect of the solvent on the one-pot conversion of xylose over Cu/SBA-15-SO₃H at 140 °C. Reaction conditions: 0.83 mmol xylose, 10 mL of the solvent, 100 mg of the catalyst, 6 h.

160 °C. The product distribution was impacted slightly by the temperature, and furfuryl alcohol was always the main product. The yields of xylitol and 2-methyl furan increased with increasing temperature. Approximately 2% yield of levulinic acid, produced from the further hydrolysis of furfuryl alcohol, was afforded at 160 °C. Therefore, 140 °C was a suitable temperature to achieve the highest furfuryl alcohol yield when considering the hindrance by the occurrence of side reactions.

Hydrogen pressure also regulated the product distribution by affecting the hydrogenation step. As shown in Fig. 8, the conversion of xylose and the yield of xylulose were almost unchanged with the increasing H₂ pressure from 1–5 MPa, while the yield of the hydrogenated product, xylitol, increased conspicuously during this period along with the attenuated yield of furfural. The yield of furfuryl alcohol reached the maximum of 62.6% at 4 MPa and declined at 5 MPa; meanwhile, a minute quantity of the over-hydrogenation product, 2-methyl furan, was detected at 5 MPa. In addition, the very different product distribution in the 3 MPa N₂ atmosphere demonstrated that furfural was the main product rather than furfuryl alcohol, accompanied by only xylulose. This result evidenced that *n*-butanol in the biphasic solvent had no significant influence on the transfer hydrogenation for the hydrogenated product formation during this 6-h process.

The effect of solvents on the product distribution was also investigated, as shown in Fig. 9. When *n*-butanol was used as the sole solvent, the conversion of xylose hardly proceeded due to the weak solubility of xylose in *n*-butanol. The highest selectivity of furfuryl alcohol was achieved in the biphasic solvent comprised of water and *n*-butanol with a volume ratio of 1:3. The continuous increase in the content of water in the biphasic solvent significantly promoted the hydrolysis of furfuryl alcohol, leading to the formation of levulinic acid in a sole water solvent and biphasic solvent comprised of equivoluminal water and *n*-butanol. Excessive water facilitated the formation of the

isomerization product, xylulose, and the occurrence of polycondensation, resulting in a decrease in the total carbon efficiency. Therefore, an adequate content of organic reagent in the biphasic solvent was applicable for the extraction of furfural and furfuryl alcohol from the aqueous phase to the organic phase, and the inhibition of side reactions such as hydrolysis and condensation, which explains the efficient productivity [43].

When the organic phase was replaced with toluene, the selectivities of both xylitol and furfuryl alcohol were lower down, while that of furfural was remarkably improved. As previously reported [43], the lower hydrogen solubility in aprotic solvents, such as toluene, compared to that in protic solvents, inhibited both the further hydrogenation of furfural and the hydrogenation of xylose. When the organic phase was replaced with isopropanol, although the extraction effect of the biphasic solvent was canceled, the selectivity of furfuryl alcohol was improved to 58%. However, the selectivity of furfuryl alcohol in isopropanol was still lower than that in the *n*-butanol solvent due to the extremely high selectivity of the by-product, xylitol. A similar rationalization reported to explain this comparison was that [12] the hydroxyl groups of the protic solvent could form a hydrogen bond with the carbonyl groups of the reactant to enhance the hydrogenation activity of the C=O bonds; however, the excessive interaction between isopropanol and the feedstock (xylose and xylulose) promoted the direct hydrogenation of xylose to xylitol, thereby reducing the selectivities of furfural and furfuryl alcohol.

4. Conclusions

In conclusion, a bifunctional Cu/SBA-15-SO₃H catalyst was designed, synthesized, and employed in the one-pot catalytic conversion of xylose to furfuryl alcohol. The acidic -SO₃H sites and Cu sites co-existed, maintained a balance, and cooperatively catalyzed the cascade conversion. The impacts of the Cu/acid ratio and mesopore size on the product distribution showed

that the excessive acidic site and large pore size could promote the xylose conversion but lead to a low furfuryl alcohol yield. The reaction conditions were optimized as follows: 140 °C, 4 MPa, and 6 h in a biphasic water/*n*-butanol solvent. A relatively high reaction temperature led to the further hydrogenation to 2-methyl furan, while a relatively high hydrogen pressure led to the side hydrogenation reaction, which produced xylitol. The biphasic solvent allowed xylose solvation as well as furfuryl product extraction. This catalytic system could be potentially applied in the one-pot production of furfuryl alcohol from hemicellulose-derived xylose.

Conflicts of interest

There are no conflicts to declare.

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Graphical Abstract

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One-pot cascade conversion of xylose to furfuryl alcohol over a bifunctional Cu/SBA-15-SO₃H catalyst

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The one-pot conversion of xylose to furfuryl alcohol over an efficient, inexpensive, and selective heterogeneous bifunctional catalyst was studied. The acidic -SO₃H sites and Cu sites co-existed, maintained a balance, and cooperatively catalyzed the cascade reaction. The pore properties and solvent played decisive roles in the product distribution as well.

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Cu/SBA-15-SO₃H催化木糖一锅转化制备糠醇

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摘要: 糠醇是一种重要的高附加值化学品, 目前工业上由含半纤维素或木聚糖的生物质原料经过酸脱水先制备糠醛, 糠醛再进一步加氢制备糠醇。在实际生产中, 这两步反应分别在不同的设备中进行, 增加了分离纯化和运输成本; 目前也很少有研究偶联这两步反应。本工作中, 我们制备了一种多功能介孔Cu/SBA-15-SO₃H催化剂用于一锅法一步转化木糖到糠醇, 并且通过X射线粉末衍射(XRD)、透射电子显微镜(TEM)、傅里叶变换红外光谱(FT-IR)、热重分析(TGA)、电感耦合等离子体发射光谱(ICP-OES)、X射线荧光(XRF)、NH₃-程序升温脱附(NH₃-TPD)和N₂物理吸附等表征检测了负载的酸和金属位点的可用性以及催化剂的物理化学性质, 优化了反应温度、氢气压力、反应时间和溶剂体系等反应条件, 研究了酸和金属位点的比例以及介孔尺寸对合成糠醇的影响。

XRD表征和TEM及HRTEM图像均表明, 在负载了磺酸和Cu之后, 均会一定程度上破坏SBA-15的形貌, 但是依然可以保持原本的有序介孔结构。XPS表明还原后的Cu主要以+1价的形式存在, 也有少量的0价和+2价。红外光谱表明磺酸基团和SBA-15载体以共价键形式紧密结合。氮气吸脱附和相关的BET和BJH计算表明, 我们的原位制备方法相比于传统浸渍法, 磺酸位点的含量提高了7倍以上。

通过对反应条件的优化, 该体系在140 °C和4 MPa H₂下可以实现62.6%的糠醇收率。过高的温度会引起产物过度加氢

生成2-甲基呋喃,而过高的压力会导致原料过度加氢生成木糖醇.合适的溶剂也是反应的关键因素,使用1:3的水/丁醇双相体系,一方面可以有效促进糖的溶解,另一方面可以有效萃取产物,保证了反应的碳平衡.

在对催化剂的筛选中发现,单独的SBA-15几乎无催化活性,Cu/SBA-15主要催化木糖加氢生成木糖醇,SBA-15-SO₃H主要催化木糖脱水生成糠醛,而物理混合的Cu/SBA-15和SBA-15-SO₃H的效率远不如双功能Cu/SBA-15-SO₃H催化剂.通过调节磺酸含量和探究产物时间曲线发现,提高酸性位点可以促进木糖转化,但是过多的酸性位点会导致结焦,降低糠醇收率.共同存在的磺酸酸性位点和铜金属位点保持平衡,协同催化串联反应进行.通过调节SBA-15的孔道结构发现,4 nm的孔道最适合反应进行,孔道过大会降低反应的整体碳收率和糠醇收率.

本催化体系实现了从木糖一锅多步法制糠醇,并对催化剂的构效关系进行了研究,对反应条件进行了系统的优化,有希望实际应用到糠醇生产中.

关键词: 生物质; 糠醇; 多相催化; 一锅法合成; 木糖

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