Enhanced formation of 5-HMF from glucose using a highly selective and stable SAPO-34 catalyst

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HIGHLIGHTS

- SAPO-34 was found to be an effective and robust catalyst in GVL/water for 5-HMF production from glucose.
- High 5-HMF yield of 93.6% from glucose was achieved.
- The presence of water (5–15 wt%) increased the yields of 5-HMF.

GRAPHICAL ABSTRACT
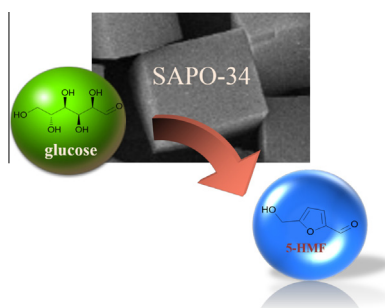
ABSTRACT

The production of 5-hydroxymethylfurfural (5-HMF) from carbohydrates is scientifically valuable but technologically challenging. In the present work, with the aim of developing an efficient and less harmful alternative to the Cr/ionic liquid system for 5-HMF production, SAPO-34 was prepared and used as the sole catalyst for the conversion of hexoses to 5-HMF in γ-valerolactone (GVL). This novel catalytic approach was quite selective for 5-HMF, affording 93.6% HMF yield from glucose at 443 K. Peculiarly, contrary to results obtained with conventional systems, the presence of water in this reaction system exhibited a positive effect on the 5-HMF yield. Moreover, SAPO-34 proved to be a robust heterogeneous catalyst that can be recycled and reused for at least five runs without significant loss of catalytic activity. The catalytic route proposed in this paper shows great potential for optimizing the catalytic process for 5-HMF production.

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1. Introduction

Waste lignocellulose materials are attracting much attention as promising new sources of energy and value-added chemicals due to their availability and abundance [1]. Recently, considerable efforts have been made to develop practical pathways to transform biomass-derived carbohydrates into a broad range of interesting compounds. 5-Hydroxymethylfurfural (5-HMF) has a versatile range of applications and is the most well-known platform chemical obtained from the chemical conversion of C_6 carbohydrates [2,3], and it has received significant attention as one of the priority chemicals on the list of "ten bio-based chemicals" published by the U.S. Department of Energy [4].

Rapid progress in the development of efficient catalytic approaches for 5-HMF production has been witnessed over the past few years [5]. Generally, fructose can be efficiently converted to 5-HMF with excellent yields by dehydration catalysts [6], such as strong acid cation-exchange resins, zeolites, or mineral acids. Unfortunately, the large-scale application of fructose for producing

5-HMF is limited by its high cost [7]. On the other hand, as the cheapest and the most abundant monosaccharide, glucose is considered the preferred starting material for 5-HMF production, although its stable pyranoside ring structure hinders the reaction efficiency. In order to promote the isomerization of glucose into fructose, the pioneering Cr/ionic liquid system and other routes based on this catalytic system have been intensively investigated [8,9]. Although these catalytic processes exhibit high catalytic activities in the synthesis of 5-HMF from glucose, the reactions are performed with toxic heavy metals and expensive ionic liquids, and the subsequent catalyst separation can also represent a major problem. To overcome these challenges, many attempts have been made to develop Cr-free methods as less harmful alternatives, and researchers have turned their attention to more promising solid acid catalysts with good thermal and chemical stability, sustainability, and environmental friendliness [10]. To date, various heterogeneous catalysts, including polymers [11], oxides [12,13], mesoporous silica [14], montmorillonites [15], zeolites [16], carbonaceous solid materials [17], and ionic liquids [18], have been exploited for 5-HMF production.

Notably, the use of acidic porous solid materials as catalyst is highly attractive due to the potential for combined acidic catalysis and shape-selective catalysis. Jiménez-Morales et al. have investigated the production of 5-HMF using various catalysts based on mesoporous MCM-41 silica containing ZrO_2; they reported that these catalysts were quite selective toward 5-HMF, with only 5-HMF detected as product, while levulinic acid and formic acid were absent [19]. Xu et al. developed a series of ordered mesoporous zirconium oxophosphates for the dehydration of fructose to 5-HMF, with M-ZrPO-0.75 leading to 97.4% fructose conversion and 79.6% selectivity for 5-HMF when using dimethyl sulfoxide as reaction solvent under relatively mild conditions [20]. Mondal et al. employed the nanoporous sulfonated polymer SPPTPA-1 with very high surface acidity for the direct conversion of sugars to 5-HMF, and attained 51.4% 5-HMF yield from sucrose [21]. Furthermore, the enhancement effect of inorganic microporous materials on the production of 5-HMF has also recently been demonstrated. Swift et al. investigated tandem glucose isomerization and fructose dehydration to 5-HMF over the bifunctional aluminosilicate zeolite BEA [22]. Furthermore, organic structure-directing agent (OSDA)-free zeolite beta with high Al content exhibited high catalytic performance in the conversion of glucose to HMF, with about 68% HMF yield obtained [23].

Among the various types of porous acid solid materials catalyzing synthetic organic reactions, silicoaluminophosphates (SAPOs) are a novel class of molecular sieves that exhibit unique structural as well as physicochemical properties such as high specific surface area, tunable acidity and pore-size dimensions, and high thermal and hydrothermal stability [24]. Within this context, SAPO-34 is considered to show promise for industrial applications in the methanol to olefins (MTO) process [25], and it has attracted considerable attention for application in other fields including selective catalytic reduction (SCR) reactions [26,27], gas adsorption [28], and the dehydration of fructose into 5-HMF [29]. In either case, in addition to the need for a robust and stable catalyst, a sustainable and efficient reaction solvent is also highly desirable for the large-scale synthesis of 5-HMF. To address these concerns, a number of different solvents including water [30,31], organic solvents [32], ionic liquids [33], and biphasic aqueous/organic solvents [34] have been developed to facilitate 5-HMF formation and minimize the occurrence of side reactions.

This manuscript describes the synthesis of SAPO-34 and its use as a catalyst to convert glucose to HMF in the biomass-based solvent γ-valerolactone (GVL). The catalytic performance and reusability of SAPO-34 for 5-HMF formation have been demonstrated and optimized. GVL is a sustainable liquid, as it is naturally occurring, nontoxic, and also has desirable properties including a high boiling point and water miscibility, but it does not form an azeotrope with water or undergo conversion to hazardous peroxides in the presence of air. This work may provide a promising strategy to access 5-HMF from glucose with high potential as a sustainable candidate for further application.

2. Materials and methods

2.1. Materials

Pseudoboehmite was purchased from Zibo Baida Chemical Company Ltd, China. D-Glucose (⩾99%) was purchased from Alfa Aesar. γ-Valerolactone (⩾98%) and colloidal silica were supplied by Sigma-Aldrich. All other chemicals were supplied by local suppliers. All of the reagents were used as received without further purification.

2.2. Synthesis and characterization of the catalyst

The SAPO-34 catalyst was synthesized by the hydrothermal method using 85% phosphoric acid as the P source, pseudoboehmite as the Al source, colloidal silica as the Si source, and triethylamine as template. The molar composition of the synthesized gel was: 1.0 Al_2O_3: 1.0 P_2O_5: 0.2 SiO_2: 3.0 Et_3N: 50 H_2O. The resulting gel was transferred to a Teflon-lined stainless steel autoclave and the solution was left to age (crystallize) for 24 h at 473 K under atmospheric pressure. The crystalline product obtained was then filtered, washed with distilled water, and dried at 373 K overnight. The material thus obtained was calcined in the presence of air at 873 K for 6 h.

The crystal size and morphology of the as-synthesized sample were determined by scanning electron microscopy (JSM-6510LV). The crystal structure of the sample was characterized by powder X-ray diffraction (XRD) working with Cu Kα radiation (λ = 0.154 nm, 40 kV, 40 mA); data ranging from 5° to 50° were collected at a step size of 0.02°.

The N_2 adsorption/desorption isotherms of the SAPO-34 sample were measured at −196 °C using an automatic ASAP 2460 system from Micromeritics to obtain the BET surface area and pore volume. Prior to the analysis, the sample was degassed under vacuum at 250 °C for 12 h. The specific surface area was determined by the BET (Brunauer–Emmett–Teller) method. The micropore volume was calculated using the Harkins–Jura model (t-plot analysis).

The temperature-programmed desorption (TPD) study of NH_3 was carried out using a TP 5000-II multiple adsorption apparatus (Tianjin Xianquan Corporation of Scientific Instruments, China). In a typical method, SAPO-34 was firstly activated at 773 K (10 K min^{-1}) in helium flow (40 mL min^{-1}) for 1 h. Next, the sample temperature was decreased to 323 K and NH_3 was adsorbed by exposing the samples to NH_3 in helium. After this adsorption process, the sample was flushed with helium gas for 1 h at 373 K for desorption of the physisorbed NH_3. Then, desorption of NH_3 was carried out in helium flow (40 mL min^{-1}).

Qualitative determination of both Brønsted and Lewis acid sites was performed by in situ FTIR (Nicolet 6700) using NH_3 as a probe molecule outgassed at 423 K.

2.3. Typical procedure for the catalytic conversion of glucose into HMF

In a typical run, GVL (1.6 g), water (160 mg), glucose (30 mg), and SAPO-34 (20 mg) were added to a 10 mL thick-walled glass reactor. The reactor was then immersed into a preheated oil bath with magnetic stirring, and the reaction mixture was stirred for a given reaction time at various temperatures. After reaching the tar-

get reaction time, the reaction was quenched by introducing the reactor into a cooled water bath. The sample was then diluted, filtered, and further employed for product analysis. For catalyst recycling tests, the SAPO-34 was separated from the reaction mixture by filtration and washed with deionized water. Subsequently, the used SAPO-34 was dried in a vacuum oven at 383 K for 12 h, and then calcined in a muffle furnace at 823 K for 5 h before being subjected to the next reaction.

2.4. Determination of the products

Quantitative analysis of HMF and glucose was performed by HPLC (Shimadzu LC-2010AHT). HMF was determined using an XDB-C18 column with an ultraviolet detector at 280 nm, and the column oven temperature was maintained at 303 K. Water/acetonitrile with a volume ratio of 85:15 was used as the mobile phase at a flow rate of $1.0 \, mL \, min^{-1}$. Glucose was determined with a refractive index detector and an Aminex HXP-87H column maintained at a column temperature of 338 K, using H_2SO_4 solution $(5 \, mmol \, L^{-1})$ as the mobile phase at a flow rate of $0.6 \, mL \, min^{-1}$. Product yields were calculated on a molar basis as follows:

$$glucose \; conversion \; (mol\%) = \frac{moles \; of \; glucose \; reacted}{moles \; of \; starting \; glucose} \times 100$$

$$HMF \; yield \; (mol\%) = \frac{moles \; of \; HMF \; produced}{moles \; of \; starting \; glucose} \times 100$$

$$HMF \; selectivity \; (mol\%) = \frac{moles \; of \; HMF \; produced}{moles \; of \; glucose \; reacted} \times 100$$

3. Results and discussion

3.1. Characterization of the catalyst

The XRD pattern of the SAPO-34 sample is shown in Fig. 1. Typical CHA structure diffraction peaks (see http://www.iza-structure.org/databases) were observed in the sample. The significant reflections of SAPO-34 appeared at $2\theta = 9.5°$, $15.9°$, and $20.5°$, which indicated that SAPO-34 was successfully prepared via the hydrothermal process. The typical morphology of SAPO-34 was revealed in the SEM images of the sample (Fig. 2); cubic crystals were well developed in the size range of 1–3 μm.
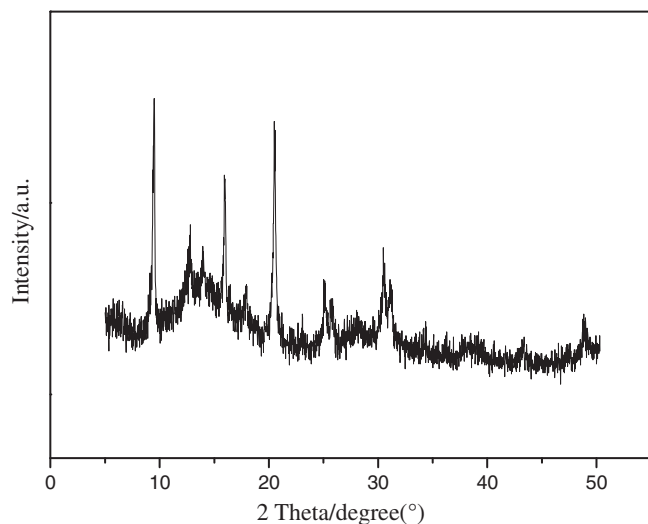
Table 1 presents the results regarding the textural characteristics and surface acidity of the obtained SAPO-34. The BET surface area and pore volume were $514 \, m^2 \, g^{-1}$ and $0.261 \, cm^3 \, g^{-1}$, respectively. The NH_3-TPD studies revealed the total acid density of the SAPO-34 sample to be $584 \, \mu mol \, g^{-1}$.

Fig. S2 depicts the FTIR spectrum obtained after adsorption of ammonia onto SAPO-34. The results showed that the sample contained two kinds of acid sites with different strengths, with the Brønsted acid sites predominating; the spectral bands at $1450 \, cm^{-1}$ and $1630 \, cm^{-1}$ were attributed to ammonia coordinated to Brønsted acid sites and Lewis acid sites, respectively.

3.2. Effect of reaction temperature on 5-HMF production from glucose catalyzed by SAPO-34

In the case of 5-HMF formation from glucose with SAPO-34 as catalyst, the reaction temperature showed a marked effect on 5-HMF yield. As depicted in Fig. 3, upon the increase of the reaction temperature from 423 K to 443 K, the peak 5-HMF yield increased correspondingly from 59.7% to 82.2%, and the time for achieving the peak value decreased from 65 min to 40 min, indicating that the higher temperature led to a more rapid peak value and higher
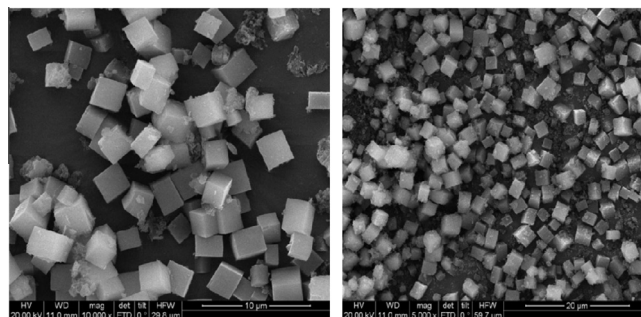
Fig. 2. SEM photographs of SAPO-34.

Table 1
Acidity and textural properties of the SAPO–34 sample.

Acid density ($\mu mol \, g^{-1}$)	Surface area ($m^2 \, g^{-1}$)	Pore volume ($cm^3 \, g^{-1}$)	Pore size (nm)
584	514	0.261	0.43

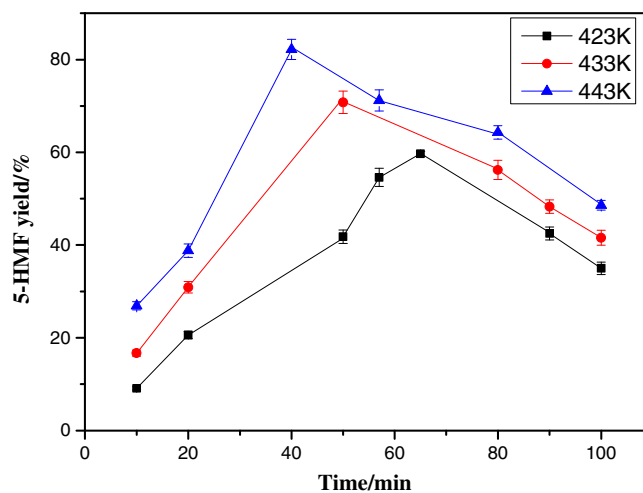**Fig. 1.** XRD pattern of the SAPO-34 synthesized.

Fig. 3. Effect of temperature on 5-HMF production from glucose in GVL using SAPO–34 as catalyst. Reaction conditions: 10 mg glucose, 1.6 g GVL, 20 mg SAPO-34.

HMF yield. However, further prolonging the residence time after the optimal time led to decreased HMF yield, mainly due to side reactions that formed unidentified soluble polymers and humins. From these data, a reaction temperature of 443 K was considered to be the optimal temperature to study other parameters of the catalytic process.

Compared with homogeneous systems, the underlying chemistries of heterogeneous catalytic systems for 5-HMF production are more complicated. Following the pioneering work of many research groups, several factors, including the type and strength of acid site, as well as the adsorption strength of the catalyst, have been identified to contribute to glucose isomerization and dehydration chemistry [35]. It is now well established that glucose isomerization to fructose takes place on Lewis acid sites [22,35,36] and the dehydration step requires Brønsted acid sites. Thus, it can be deduced that the bifunctional properties of SAPO-34, which contains a sufficient number of both Lewis and Brønsted acid sites, facilitates the cascade reactions in the glucose conversion process. Furthermore, small-pore molecular sieves (such as SAPO-34) may offer higher 5-HMF selectivity because small pore sizes can lead to fewer side reactions [37].

Additionally, it is very much worth noting that the solvent mediates glucose conversion, because no satisfactory 5-HMF yield can be achieved using water as reaction medium (Table S1). Thus, the high 5-HMF yields in Fig. 3 could be assisted by the presence of GVL, which solubilized the degeneration compounds formed during the process. GVL is typically considered as a promising renewable solvent derived from biomass and has recently attracted interest for improving the production of furanic compounds by biomass conversion [38]. The excellent solubility of GVL is beneficial to reduce the deposition of organic compounds in the cavities of SAPO-34 and to slow down the blocking or poisoning of the catalytic sites by the adsorption of carbonaceous compounds on the catalyst surface.

3.3. Effect of water content on 5-HMF production from glucose in the presence of SAPO-34

Fig. 4 shows the representative reaction profiles of 5-HMF formation at various water contents in the range of 5–15 wt% (dosage weight ratios are based on GVL). Surprisingly, the presence of water in this catalytic system pushed the reaction toward 5-HMF formation, and higher 5-HMF yields were obtained compared with the treatments without added water (Fig. 3). It is usually believed

Fig. 4. Effect of water concentration on 5-HMF production from glucose in GVL catalyzed by SAPO-34. Reaction conditions: 10 mg glucose, 1.6 g GVL, 20 mg SAPO-34, 443 K.

that the presence of water has a negative effect on 5-HMF formation because water has the potential to accelerate possible side reactions such as the rehydration of 5-HMF into levulinic acid and formic acid. However, contrary to previous observations, the presence of water in our catalytic system resulted in increased 5-HMF yield, and similar results have been obtained in other research into the production of furfural (a sister chemical to 5-HMF) in GVL or γ-butyrolactone (BVL) [39,40]. However, no mechanistic rationale for this abnormal phenomenon has been presented to date. One possible explanation is that GVL is completely miscible with water; thus, the reaction mixture acts in a similar fashion to numerous micro-biphasic systems in which the organic phase extracts 5-HMF in situ and prevents its decomposition and cross-polymerization. In addition, 5-HMF yields showed a tendency to decrease at these three water concentrations when further prolonging the residence time, but the gradual downward trend was less severe than those without water added (Fig. 3), mainly due to the stability of 5-HMF in GVL/water mixtures under the applied conditions. The abnormal effect of water on 5-HMF formation in this catalytic system is very interesting and worth further exploration in the future.

Interestingly, formic acid and levulinic acid were not detected; thus, the decrease in 5-HMF yield may have been caused by the preferential condensation and polymerization of 5-HMF into other undesired byproducts such as soluble polymers and humins, or by hydration of 5-HMF through a mechanistic route distinct from that leading to levulinic acid and formic acid [41]. Similar results have also been observed recently in reaction systems involving functionalized silica nanoparticles in water/DMSO [42], vanadyl phosphate in water [43], and magnetic lignin-derived carbonaceous catalyst in DMSO [44]. Moreover, the 5-HMF yields obtained at 10 wt% water concentration were comparable to those obtained at 15 wt% water concentration; thus, 10 wt% water concentration was selected for the following treatments.

3.4. Effect of catalyst dosage on 5-HMF production from glucose

Using the optimized temperature of 443 K and employing GVL/H$_2$O as reaction medium, the effect of catalyst loading on the conversion of glucose into 5-HMF was then evaluated, and the results are summarized in Fig. 5. Catalyst loading played a critical role in the reaction of glucose conversion into 5-HMF. The variation of the amount of catalyst (5–50 mg) showed the highest 5-HMF yield of 93.6% and a glucose conversion of 100% with a SAPO-34 dosage of 20 mg after 40 min. Progressive increases in both glucose conversion and 5-HMF yield were observed with an increase in catalyst loading up to 20 mg, which may be attributed to an increase in the number and availability of catalytically active sites. Beyond this point, the 5-HMF yield decreased upon further increasing the catalyst loading under the typical conditions, mainly because the excess SAPO-34 facilitated side reactions, especially the excess Lewis acid sites, which inevitably promoted the degradation reactions [45,46] and led to the formation of undesired compounds.

3.5. Effect of glucose concentration on 5-HMF production from glucose

From an industrial point of view, it is of great interest to be able to conduct these reactions at a relatively high glucose concentration to achieve a more economical and sustainable process; thus, the effect of glucose concentration on glucose conversion and 5-HMF yield was investigated and these results are presented in Fig. 6. The 5-HMF yield and selectivity were roughly stable upon increasing the glucose concentration from 10 mg to 40 mg, with 5-HMF yields in excess of 90% obtained. However, when conducting the reaction with 50 mg and 60 mg glucose concentration under the typical reaction conditions, the 5-HMF yield and glucose
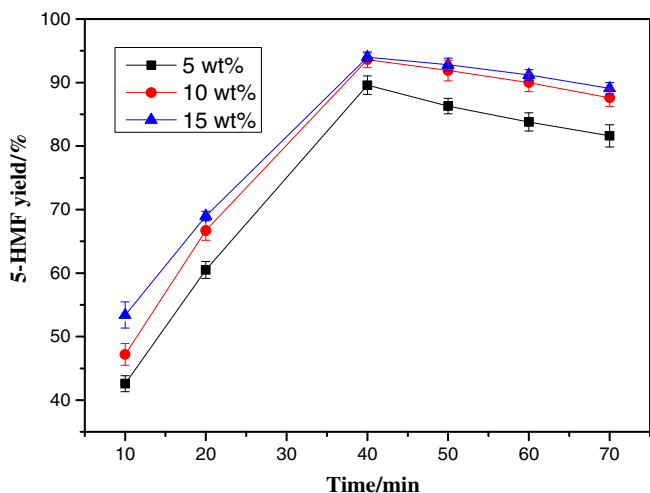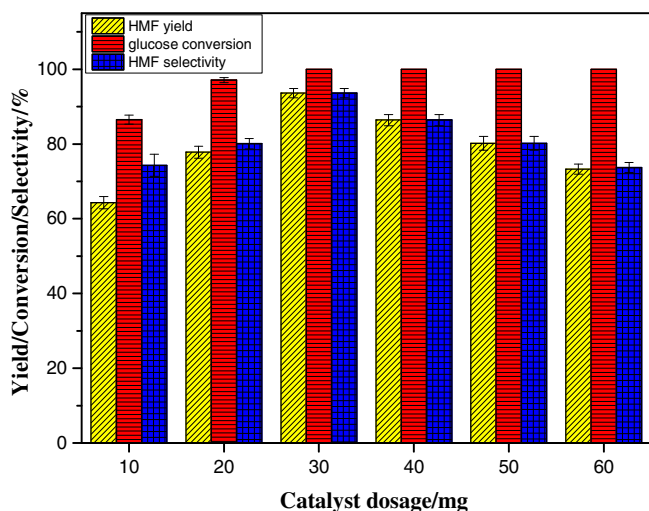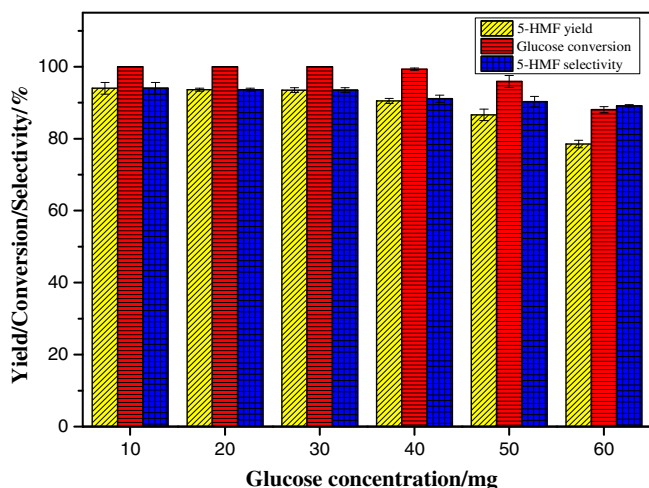
Fig. 5. Effect of catalyst dosage on 5-HMF formation from glucose in GVL containing 10 wt% water using SAPO-34 as catalyst. Reaction conditions: 443 K, 10 mg glucose, 20 mg SAPO-34, 40 min.

Fig. 6. Effect of glucose concentration on 5-HMF production in GVL containing 10 wt% water using SAPO-34 as catalyst. Reaction conditions: 443 K, 20 mg SAPO-34, 40 min.

conversion gradually dropped. The reduced yields of 5-HMF at high initial glucose concentrations were possibly due to the formation of a higher amount of humin compounds from the intermediates (or glucose) with 5-HMF. This hypothesis was supported by the solution color change from light yellow to dark brown by the end of the reaction. This color change can be ascribed to the formation of condensation and cross-polymerization products, mainly polymers and soluble humins. Furthermore, taking into consideration 5-HMF yield, selectivity, and potential industrial applications, a 40 mg initial glucose concentration was thought to be advisable, which corresponded to a glucose/SAPO-34 weight ratio of 2:1. Additionally, this catalytic system was also effective for the conversion of fructose and sucrose to 5-HMF (Table S2); the use of SAPO-34 alone in GVL/water gave >90% yields of HMF from fructose and sucrose.

3.6. Mechanism of 5-HMF formation in GVL/water system catalyzed by SAPO-34

5-HMF showed high stability in our reaction system without adding sugar reactants (Fig. S3); thus, the rehydration of 5-HMF to levulinic acid and formic acid was not included in the reaction pathways. The high yield of 5-HMF is a synergetic effect of the multifunctional catalyst and the excellent reaction solvent. The 5-HMF yield of approximately 90% from glucose confirmed that both Brønsted and Lewis acid sites on SAPO-34 were sufficiently active for the successive reaction steps in these treatments. We proposed a reaction network of glucose conversion to 5-HMF over the SAPO-34 catalyst in GVL/water, as shown in Scheme 1, including two steps: (1) isomerization of glucose to fructose by Lewis acid sites on the synthesized SAPO-34; (2) further dehydration of the generated fructose to 5-HMF by Brønsted acid sites. On the other hand, no obvious insoluble humins were observed because GVL solubilized most of the by-products, and minimized the side reactions. Besides, the rehydration of 5-HMF is inhibited in this reaction system, thereby allowing the realization of highly selective 5-HMF production directly from glucose.

3.7. Performance of the recycled SAPO-34 in 5-HMF formation

Catalyst reusability and stability are extremely vital to evaluate the efficiency of heterogeneous catalytic systems according to the principles of green and sustainable chemistry, and also contribute to reducing the production costs in the practical transformation of
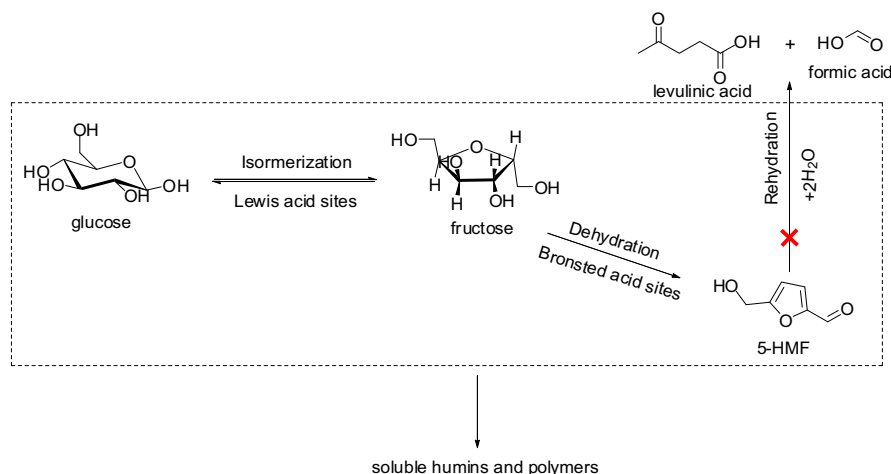
Scheme 1. Possible pathways for converting glucose to 5-HMF in a GVL/water system on SAPO-34.
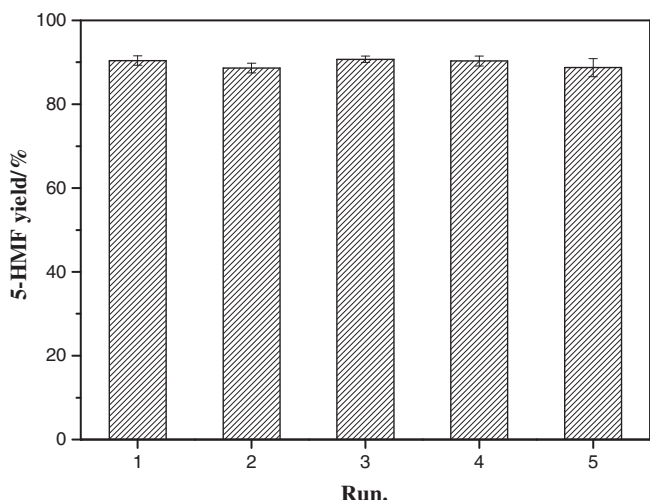
Fig. 7. 5-HMF yields over SAPO-34 in cycle usage test. Reaction conditions: 1.6 g GVL with 10 wt% water, 40 mg glucose, 20 mg SAPO-34, 443 K, 40 min.

glucose into 5-HMF. In the present work, SAPO-34 was refreshed according to the procedure in Section 2.3, and the recovered SAPO-34 was added to fresh GVL/water solvent and used for the next reaction run. As depicted in Fig. 7, comparable activities were observed both before and after five cycles of catalyst regeneration, which suggested that the catalytic activity of SAPO-34 can be restored. Thus, SAPO-34 is preferable for glucose dehydration from the viewpoint of catalyst durability.

4. Conclusions

The utilization of SAPO-34 in GVL/water medium was found to lead to excellent catalytic performance for 5-HMF production from glucose, fructose, and sucrose. Under the optimal reaction conditions, 100% glucose conversion and 93.6% 5-HMF yield were obtained using a glucose/catalyst weight ratio of 2:1 after 40 min of reaction at 443 K. More importantly, the presence of water in the range of 5–15 wt% along with GVL improved the 5-HMF formation. The system of SAPO-34 in GVL/water afforded remarkably high yields of HMF from glucose, which was probably due to the advantages of (i) GVL/water mixtures minimizing the side reactions involving 5-HMF and thereby increasing selectivity toward HMF, and (ii) facile isomerization of glucopyranose to fructofuranose by the bifunctional SAPO-34 catalyst containing both Lewis acid and Brønsted acid sites. Furthermore, SAPO-34 was shown to be a robust and reusable catalyst that could be reused at least five times without significant loss of activity, which confirmed the potential of the approach described in this study for further application.

Acknowledgements

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cej.2016.09.003.

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