ORIGINAL PAPER



Application of vanadyl hydrogen phosphate/KIT-6 composites as a catalyst for dehydration of sucrose

Jaleh Najafi Sarpiri¹ · Alireza Najafi Chermahini¹ · Mohammad Saraji¹ · Ali Shahvar¹

Received: 26 October 2020 / Accepted: 21 January 2021 © Iranian Chemical Society 2021

Abstract

In this research work, the synthesis of well-ordered mesoporous structure KIT-6 silica-supported vanadyl hydrogen phosphate hemihydrate (VHP/KIT-6) catalysts possessing varying surface area was carried out, followed by being utilized in the dehydration of sucrose to 5-hydroxymethylfurfural (5-HMF) as a solid acid catalyst. The fabrication of two different VHP/KIT-6 catalysts was conducted using the impregnation approach through V_2O_5 reduction in alcoholic media. Then, the catalytic behavior presented by the prepared VHP/KIT-6 samples was compared with unsupported VHP and unsupported vanadyl pyrophosphate (VPP), which was prepared through the calcination of VHP precursor at 400 °C for 24 h. The prepared catalysts were characterized by different analyses, including ICP-OES, BET, XRD, NH₃-TPD analysis, FT-IR spectroscopy, as well as SEM and TEM techniques. Furthermore, important parameters, including the catalyst type and weight, sucrose amount, time, temperature, and the type of solvent on sucrose dehydration, were also studied. It was observed that the high-est catalytic activity in the dehydration reaction (5-HMF yield: 67%, sucrose conversion: > 94%) could be provided by the catalyst possessing the highest surface area. Moreover, the catalyst reusability was examined for consecutive four times, based on which no considerable change in the catalytic activity was observed.

Keywords Mesoporous KIT-6 silica · Vanadyl hydrogen phosphate hemihydrate catalyst · Sucrose dehydration · 5-hydroxymethylfurfural · Biomass conversion

Introduction

Over the past decades, finding alternative chemicals and energy sources has become the center of attention as a result of depletion in fossil resources. It seems that biomass as a source of renewable energy can be considered appealing for several reasons, the most important of which are its abundance and inexpensiveness. Biomass is provided by numerous sources, including wastes of wood, animal, farm, forestry, agriculture, and industry. Biomass-derived carbohydrates can be converted to different chemical platforms [1–3] and used in the catalysis [4–6]. 5-Hydroxymethylfurfural is considered as one of the most critical bio-based product opportunities from carbohydrates, as one of the top ten materials with the most valuable platform chemicals [7]. 5-HMF possesses numerous applications in different industries,

Alireza Najafi Chermahini anajafi@iut.ac.ir; najafy@gmail.com e.g., construction, textile, packaging, cosmetics, health, and food as an essential building block in numerous fields such as (1) effective natural ingredient in healthy foods [8-10]; (2) precursor of furan-2,5-dicarboxylic acid and its polymer polyethylene furanoate [11-13]; and (3) formaldehyde replacement in adhesives and resins [14–16]. Dehydration of numerous C6 carbohydrates, including monomeric and polymeric ones, e.g., sucrose, glucose, maltose, fructose, cellulose, starch, and inulin, can be utilized as an efficient method for the synthesis of 5-HMF, among which sucrose, the most abundant one [17], can be the more appropriate choice to produce 5-HMF industrially. One D-glucose and one D-fructose are the components composing sucrose disaccharide. It is noteworthy that, before dehydration, di- and polysaccharides must be hydrolyzed into the related monosaccharides. Besides, the first step isomerization of fructose must be carried out for glucose monomers. Therefore, hydrolysis, isomerization and dehydration are the reactions, which make up the reaction mechanism, which has proved complicated because of degradation of 5-HMF to formic and levulinic acid or polymeric species, known as humins.

¹ Department of Chemistry, Isfahan University of Technology, 84154-83111 Isfahan, Iran

Today, catalytic dehydration of sucrose to 5-HMF is the subject of numerous investigations. For instance, Jain et al. made use of zirconium phosphate (ZrP) as a catalyst to synthesize 5-HMF from sucrose, carried out in a sealed reactor, which resulted in a 52% 5-HMF yield in H₂O-diglyme [18]. In another study, Marullo et al. utilized HY zeolite in imidazolium-based IL mixtures to dehydrate sucrose to 5-HMF, carried out at 120 °C for 3 h, which led to a 62% 5-HMF yield [19]. Li et al. also reported the dehydration of sucrose to 5-HMF by using yeast-derived carbonaceous microspheres in the ionic liquid of 1-butyl-3-methylimidazolium chloride, through which a 44.8% 5-HMF yield could be provided [20]. Numerous investigations have also been reported in aqueous media with ZnCl₂[21], CrCl₃ [22] and WCl₃ [23] catalysts. Nevertheless, all the above-mentioned catalytic systems suffer from a variety of demerits including corrosion, the use of toxic solvents, the harmful effects of chromium ion on the environment, high costs, difficult reusability in the utilization of mineral acids along with costly multi-step synthesis procedure of ionic liquids [24].

Vanadium phosphate oxide (VPO) catalyst, a layered material, in addition to oxidation [25, 26] and desulfurization [27] catalysis, has also attracted a great amount of attention in some solid acid-catalyzed reactions, including acetic acid esterification [28] and dehydration of glycerol [29, 30], fructose [31, 32], glucose [33, 34] and xylose [35]. Vanadyl hydrogen phosphate hemihydrate VOHPO₄.0.5H₂O (VHP), with Brønsted and Lewis acid sites, has been employed in the catalytic dehydration of carbohydrates [33, 35, 36], which has proved outstanding to be adopted as a catalyst for dehydration of carbohydrates to 5-HMF. Kamiya et al. reported the study of both Lewis and Brønsted acid behavior of activated VPO catalysts [37]. They found out that VPO acidic properties were mostly dependent on its preparation strategy, indicating that an organic medium could be much more appropriate when compared to an aqueous one. In another study, Feng et al. reported the fabrication of three types of VPO catalysts, carried out in mixed *iso*-butyl and benzyl alcohols, single benzyl alcohol and the presence or absence of polyethylene glycol-6000 [38]. They indicated that VPO in the presence of PEG-6000 and mixed iso-butyl and benzyl alcohols were capable of providing higher acidic properties. Wang et al. investigated the catalytic performance of VHP and VPP in glycerol dehydration and reported that VHP is more active than VPP in the reaction [36].

Nanoporous materials can be applied with other functional groups to increase their performance by balancing hydrophobicity, acidity and basicity [39–45]. Most nanoparticles are usually formed inside channels that the porous supports prevent them from agglomeration [46]. The KIT-6 mesopores, with tridimensional symmetric cubic structure Ia3d and a bicontinuous interpenetrating network [47–51], supplied direct access to the active sites, leading to an enhancement in the insertion or diffusion of species into the KIT-6 interior [52]. Herein, we decide to firstly graft VPO materials onto high surface area mesoporous silica KIT-6 (impregnation technique) and then study the effect of the type and amount of acid sites of different loadings of VPOs onto KIT-6 in the conversion of sucrose to 5-HMF. Besides, the effects of various experimental parameters, including reaction type and dosage of the catalyst, temperature, time, type of solvent, reusability, and carbohydrates amount and type, have been investigated in this research to achieve the significant catalytic behavior.

Experimental

Materials

 V_2O_5 , PEG-6000 (Riedel–de Haen), and H_3PO_4 (Merck Co., 85%) were utilized for the fabrication of VHP. Triblock copolymer P123 (EO₂₀PO₇₀EO₂₀, M=5800, Aldrich Co.), tetraethylorthosilicate (TEOS > 98%, Dae-Jung, S Korea.) and *n*-butanol (Merck Co.) were employed for the preparation of the mesoporous silica KIT-6. Merck Co. supplied glucose, fructose, maltose and sucrose for the dehydration process. All the solvents utilized for the dehydration reaction (DMSO, THF and NMP) were also purchased from Dae-Jung, S Korea. The reagents were utilized as received with no purification.

Characterizations

The FT-IR analysis was carried out with potassium bromide (KBr) disks by using a Bruker Tensor 27 Fourier transform infrared spectrometer. Energy-dispersive X-ray spectroscopy was employed as an spot elemental analysis to evaluate the composition of the optimum catalyst. ICP-OES analysis was utilized to study the elemental analysis, done by using an inductively coupled plasma optical emission spectroscopic (ICP-OES, 5300DV, PerkinElmer). The crystalline structure of the prepared catalysts was conducted by X-ray diffraction (XRD) analysis, an Asenware XDM-300 diffractometer, using Ni-filtered Cu K α radiation ($\lambda = 1.54$ Å), and the results were studied concerning the ICDD database by using XPert High score v0.3 software. Field emission scanning electron microscopy (FESEM), FEI Quanta 450 microscope, and transmission electron microscopy (TEM), a Philips EM 208S instrument, were both utilized to perform the morphological studies on the optimum catalyst. The nitrogen adsorption/desorption isotherms were employed at 77.0 K on a BELSORP MINI II to determine the textural parameters of the prepared catalysts, which had been outgassed at 120 °C for 2 h before the analysis. For NH₃-TPD measurements, a Nanosord NS91 (Sensiran Co., Iran) apparatus was utilized to perform the temperature-programmed desorption with NH₃. To eliminate not only the adsorbed moisture but also impurities, all the prepared catalysts (0.05 g) were degassed in a flow rate of 10 mL/min He, which was carried out at 300 °C for 1 h before the analysis. Subsequently, the prepared catalysts were saturated with 5% NH₃/He at 110 °C for 0.5 h. Afterward, to eliminate physisorbed ammonia, the catalysts were purged in a He stream at 110 °C for 30 min, followed by being heated from room temperature to 800 °C at a heating rate of 10 °C/min. The conversion of carbohydrates was evaluated via a high-performance liquid chromatography (HPLC) instrument, which was equipped with a refractive index detector (RID 6A, Shimadzu Corporation), and a Hector-M NH₂ column (150 mm × 3.9 mm i.d., 3 µm; RStech Co., Dae-Jong, Korea) attached to a C18 guard column. The 5-HMF yield was also analyzed by using an L-3000 RIGOL instrument (Beijing, China) which was equipped with a UV-Vis detector and a PerfectSil Target ODS-3 column (150 mm × 4.6 mm i.d., 5 µm, MZ-Analysentechnik GmbH, Germany) connected to a C18 guard column (10 mm×4 mm i.d., 5 µm). A solution containing water and methanol (90:10 v/v) was utilized as the mobile phase at a flow rate of 1 mL/min, and the detection was performed at 284 nm.

Catalysts synthesis

Synthesis of silica KIT-6

The mesoporous silica KIT-6 was prepared according to the method reported by Kleitz et al. [53]. Briefly, 4 g of poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) (P123) was first dissolved in an aqueous solution containing 144 mL of deionized water and 9.9 g of 35 wt % HCl, followed by the addition of 4 g of *n*-butanol at 35 °C. After the 1 h stirring, TEOS (6.8 g) was added at once and stirred at 35 °C for 24 h. Subsequently, the mixture was transferred to a glass bottle with a polypropylene lid

mixture was dried and filtrated at 100 °C overnight. Finally, the surfactant was eliminated by using a brief washing with a mixture of ethanol/HCl, followed by calcination at 550 °C for 6 h.

Synthesis of VPO/KIT-6 catalysts

The synthesis of the VPO catalysts was also carried out according to the literature, as reported previously [54]. Vanadium pentoxide (0.5 g) was first dissolved in a mixture of benzyl alcohol and 2-butanol (in a ratio of 1:1) as the reducing agent, followed by being refluxed at 140 °C for 5 h under stirring in order to reduce vanadium ions. Subsequently, PEG-6000 (0.15 g) and KIT-6 (0.25 and 0.50 g) were added to the prepared mixture. One hour later, the dropwise addition of H₃PO₄ (85%, 0.45 mL) was carried out to attain a P/V atomic ratio of 1.2, followed by being refluxed for 6 h. The prepared mixture was filtrated, washed and dried at 120 °C overnight until a gray-blue precipitate (VHP/KIT-6) was obtained. The VHP/KIT-6 s containing 0.25 and 0.50 g KIT-6 were labeled as VK2 and VK1, respectively, according to the V₂O₅/KIT-6 weight ratio. In comparison, the VHP phase without KIT-6 support was also synthesized and calcined so that the VPP phase could be prepared. Here, VHP and VPP materials are labeled as VH and VP, respectively.

Catalytic activity studies

All the catalytic experiments were performed in a reflux system, sand-bath and under stirring. The above system was loaded with sucrose (150-300 mg), catalyst (5-20 mg) and solvent (4 mL) at specified temperatures and times. At the end of the reaction, the mixture was centrifuged so that the catalyst could be isolated, followed by being diluted and analyzed by using an HPLC instrument. The reaction pathway for the dehydration of sucrose is depicted in Scheme 1. Additionally, the carbohydrate conversion and 5-HMF yield were calculated as follows:

Grankersion af 100 bohid 24 fr (Try (Initial har bat har bat at the transformation)/Initial carbohydrate × 100



Scheme 1 Schematic illustration of the transform of sucrose into 5-HMF and side-products

 Table 1
 Elemental analysis and textural parameters provided by the mesoporous KIT-6 and catalysts

Code	$S_{BET}^{\ \ a}(m^2g^{-1})$	$V_P^{\ b} (cm^3 g^{-1})^*$	$d_p^{\ b}(nm)^*$	$\%V^{c}$	%P °
KIT-6	549	0.46	6.30	_	_
VK1	162	0.20	6.24	11.8	14.0
VK2	100	0.18	6.24	17.8	21.1
VH	29	0.17	24.48	22.9	27.5
VP	32	0.19	10.58	-	-

^aFrom BET,

^bFrom BJH,

^cFrom ICP-OES

HMF Yield % = Produced HMF/Initial carbohydrate $\times 100$

Results and discussion

Elemental analysis by ICP-OES

Evaluation of the actual contents of vanadium and phosphorous in the prepared catalysts was carried out by using the ICP-OES technique, as shown in Table 1. It was indicated that the phosphorous- to- vanadium ratio in the prepared catalysts was 1.2, in agreement with the theoretical values of a bulk P/V ratio.

FT-IR Spectroscopy

FT-IR spectroscopy was employed to study the functional groups of the prepared catalysts, as exhibited in Fig. 1. As can be seen in the pure KIT-6 spectrum, the peaks observed at 1078, 800 and 460 cm^{-1} can be related to the asymmetric and symmetric stretching and bending bands of O-Si-O, respectively [55]. In addition to the peaks observed at 600 and 1300 cm⁻¹ in the VH and VHP/KIT6s spectrums, which are assigned to V-O and P-O stretching bands, the peaks below 1600 cm⁻¹ can also be related to O-V-O and O-P-O bending modes. The FT-IR spectra detect 1200, 1104 and 1054 cm⁻¹ (ν_{as} , PO3), 1132 cm⁻¹ (δ_{in} , P–OH), 980 cm⁻¹ (ν , V=O), 931 cm⁻¹ (ν , P–OH), 684 cm⁻¹ (ω , coordinated H_2O), 642 cm⁻¹ (δ_{oop} , P–OH), 548, 534, 480 and 417 cm⁻¹ (δ , OPO) bands which corresponds to the VHP phase [56]. The band, which has appeared at about 3400 cm^{-1} , can be related to the interlayer free structural water and the water molecules which coordinate to vanadium in the structure. Moreover, the bending modes of water molecules can also be observed at about 1630 cm^{-1} [57]. Increasing loading amount, the peaks intensities of phosphate (P-OH,OPO and PO₃) and vanadyl (V = O) groups



Fig. 1 FT-IR spectra of the VHP/KIT-6 catalysts, unsupported VHP, and pure KIT-6 $\,$

increased (VH > VK2 > VK1). In addition, the FT-IR spectrum of initial material V_2O_5 (Fig. S1) demonstrated high intensities vibrations bonds of V = O and VOV. Also, the FT-IR spectrum of calcined VPO (VP) is exhibited in Fig. S1.

XRD patterns

The low-angle XRD patterns of KIT-6 and VHP/KIT-6 catalysts are shown in Fig. 2a. It is evident that, for the pristine KIT-6, the sharp peak at $2\theta = 1.07^{\circ}$ and the two broad peaks at $2\theta = 1.73^{\circ}$ and 1.94° can be assigned to the (211), (420) and (431) planes, respectively, demonstrating the characteristic of considerably ordered three-dimensional cubic space group *Ia3d* symmetry present in the mesoporous structure of silica KIT-6 [58]. For the VHP/KIT-6 catalysts, the intensities of the peaks decrease when the loading amounts of VHP on KIT-6 increase, arising from the partial filling of KIT-6 pores via VHP species, whereas the cubic *Ia3d* symmetry of the silica can be simultaneously preserved. In the cases of V₂O₅, VH and VP (Fig. S2), there are no peaks related to mesoporosity.

The wide-angle XRD patterns of VPP, VHP, VHP/KIT-6 catalysts are presented in Fig. 2b. Both the planes and peaks of all the patterns except VP are shown in Table 2, well-matched with the crystalline phase of VOHPO₄ $0.5H_2O$ [ICDD Card No 01–084-0761]. For the VP phase, it is clear that the reflections correspond to the monoclinic (VO)₂P₂O₇ phase (ICDD Card No 00–041-0380). Moreover, the broad peak present at about 23° can be related to the amorphous structure of silica. In the case of lower intensities for VP (inset graph in Fig. 2b) vs VH, it is due to thinner crystallites



Fig. 2 a Low-angle XRD patterns of VHP/KIT-6 catalysts and pure KIT-6 and ${\bf b}$ wide-angle XRD patterns of VPO-based catalysts

of VP after activation [59]. The V_2O_5 pattern (Fig. S3) corresponds to the pattern of orthorhombic vanadium oxide (ICDD Card No 01–072-0598).

N₂ adsorption-desorption analysis

Nitrogen adsorption–desorption analysis was employed to study both the textural characterization and porosity measurements of the prepared catalysts and pristine KIT-6, as shown in Table 1 and Fig. 3. As can be seen in Fig. 3, it is evident that the graphs of the supported VHP catalysts and mesoporous KIT-6 confirm the type IV isotherms exhibiting a sharp capillary condensation step at a rather pressure range of 0.6–0.8 P/P0 as well as a typical H1 hysteresis loop of mesoporous structures possessing a considerably uniform pore size distribution. Also, it was indicated that no changes were observed in the type of the hysteresis loops after surface modification of mesoporous silica KIT-6, demonstrating that the mesoporous structure of supported VHP could be maintained. Conversely, as can be observed in Table 1, the pore volume and surface area of the prepared catalysts decreased gradually, depicting that VHP species could be introduced to the interior pores of mesoporous silica KIT-6. Furthermore, as exhibited in the pore size distribution profiles, negligible changes were observed in the average pore diameter when compared to the pure KIT-6 mesoporous silica.

The hysteresis loops present in the isotherms at $0.7 < P/P_0 < 1.00$ are generally related to the slit-shaped pores, usually observed on the aggregates, including plate-like particles [60]. By drawing a comparison between the unsupported and supported VPO catalysts, it was found that an enhancement in the specific surface area, a reduction in the diameter of the average pores and an unchanged total pore volume could be observed.

SEM and TEM analysis

The characterization of the morphology, along with the elemental analysis of the VK1 catalyst, was carried out by using FESEM–EDX and TEM analyses. By investigating the FESEM images of VK1 (Figs. 4a, b), it can be indicated that the VK1 sample presents the rosette type morphology with irregular plate-like petals. The investigation of the elemental distribution of vanadium (V), phosphorous (P) and oxygen (O) over mesoporous silica was also conducted by using EDX analysis (Fig. 5).

According to TEM images of VK1 exhibited in Fig. 4c, the VK1 sample possesses rhomboid-shaped and layered platelets, which have been stacked together on top of each other. The plate-like layers in this morphology are regarded as the typical characteristic of VPO materials [61]. In addition, some TEM images is presented in Fig. S4.

Table 2 The position of peaksand planes of VHP phase

No	1	2	3	4	5	6	7	8	9	10	11
2θ (degree)	15.57	19.57	24.4	27.13	28.81	30.49	32.17	37.42	47.92	49.17	63.25
Planes (h k l)	001	101	021	121	201	130	031	040	241	400	510
d-spacing	5.69	4.51	3.67	3.29	3.10	2.93	2.79	2.40	1.90	1.85	1.46



Fig. 3 The nitrogen adsorption-desorption isotherms of supported and unsupported VPO and pure KIT-6 and BJH profiles of VHP/KIT-6 catalysts and pure KIT-6

NH₃₋TPD

NH₃-TPD analysis made it possible to evaluate the acidic properties of the synthesized VPO-based catalysts. The NH₃-TPD profiles depicted a main peak at about 400 °C attributed to the moderate acid sites (Fig. 6). The total acidity order of the VPO-based catalysts and pure support is VH>VK2>VK1>VP>KIT-6, as the summed peak areas of NH₃-TPD profiles has been presented. As expected, a very weak peak of NH₃ desorption was exhibited by the silica mesoporous KIT-6 because of its appreciably weak acidity. For the supported VHP catalysts, it was indicated that the acidic properties increased through increasing the VHP loading amount. Furthermore, the uncalcined VPO was found to possess higher total acidity in comparison with the calcined VPO.

Catalytic performance

The efficiency of the prepared catalysts was evaluated by the dehydration reaction of sucrose, as the most abundant disaccharide, to 5-HMF. The effect of various parameters on the reaction was studied. Scheme 2 schematically depicts the plausible mechanism for the reaction, which is comprised of hydrolyzation, isomerization and dehydration. First, sucrose is hydrolyzed rapidly to fructose and glucose, and subsequently, the formed fructose is converted to 5-HMF. The conversion of glucose, nevertheless, is carried out at a lower rate because of the isomerization to fructose before dehydration [62]. Lewis acids are capable of catalyzing the glucose isomerization to fructose through facilitating the hydride shift, as isomerization catalysts [63]. Therefore, vanadium, functioning as a Lewis acid, and the two adjacent hydroxyl groups of glucose form a five-member chelate ring. Another possible pathway is a direct conversion of glucose into 5-HMF via 3-deoxy-D-glucosane [62], but







Fig. 5 EDX spectrum and elemental distribution maps for the VK1 sample



Fig. 6 NH₃-TPD profiles of VPO-base catalysts and pure KIT-6

glucose isomerization is more probable in the presence of Lewis acid [64].

Then, the fructose dehydration route is followed by water elimination, which takes place at the C-2 position of D-fructofuranose, to prepare a tertiary carbocation. Finally, it is followed by the next two β -dehydration steps, leading to the formation of 5-HMF [1].

The effect of the catalyst type

The effect of the amount of VHP loaded on KIT-6 and also unsupported VHP and VPP in the sucrose dehydration to 5-HMF was studied, as represented in Fig. 7a. The results show that VK1 with a lower loading amount is effective in catalytic activity. It seems that two parameters can affect the higher catalytic activity: surface area and surface acidity. The higher surface area as a result of the lower loading amount of VHP causes a higher 5-HMF yield. Conversely, higher surface acidity, as a result of higher loading amount of VHP, results in lower 5-HMF yield, arising from an increase in unwanted rehydration and polymerization reactions. Accordingly, the VK1 catalyst with lower surface acidity, higher surface area and lower loading of VHP is capable of providing higher catalytic activity in comparison with the VK2 catalyst and unsupported VHP. Also, it can be observed that uncalcined VPO with higher total acidity possesses a little higher 5-HMF yield compared with calcined VPO. Furthermore, the negligible 5-HMF yield without catalysts in the reaction confirms a high catalytic activity in the dehydration reaction.

The effect of the sucrose to catalyst weight ratio (S/C)

The effect of S/C on sucrose dehydration was also studied in this study, as shown in Fig. 7b. According to the obtained results, it was found that 5- HMF yield decreased under higher acidity, arising from the production of unwanted products, including levulinic acid, formic acid and humins. Hence, S/C of 20 (10 mg VK1 for 200 mg sucrose) was selected as the optimum catalyst weight and acidity amount. It was observed that the sucrose conversion could be almost accomplished (>90%) at different sucrose to catalyst weight ratios.

The effect of temperature

The effect of temperature (130 °C to 190 °C) on the 5-HMF yield and sucrose conversion was investigated, as can be seen in Fig. 7c. It can be observed that an increase in temperature has led to a significant effect on the reaction. By increasing temperature to 170 °C, the 5-HMF yield was rapidly enhanced. Nonetheless, at higher temperatures, the 5-HMF yield decreased because of the humins formation, which was confirmed by the darker color of the mixture. However, the conversion of sucrose changed insignificantly with the increasing temperature.

The effect of reaction time

The performance of the VK1 catalyst in the sucrose dehydration was studied in a variety of reaction times (30 to 75 min). As depicted in Fig. 7d, it was demonstrated that the 5-HMF yield rose to 62% after 60 min, and after that, it decreased, arising from the formation of more humins and covering active sites of the prepared catalyst. The conversion of sucrose by the VK1 catalyst could be almost completed (>94%) after 75 min.

The effect of sucrose concentration

The behavior of the VK1 catalyst in the dehydration reaction was investigated in different sucrose concentrations (Fig. 7e). It was confirmed that the sucrose conversion could be almost accomplished (>92%) in various sucrose concentrations. Nevertheless, it was indicated that the 5-HMF yield increased rapidly with the concentration increasing up to 250 mg. However, at higher dosages, due to the acceleration of humins formation, it decreased [65].

The effect of solvent

The effect of different solvents, including DMSO, NMP, H_2O and H_2O/THF , on the performance of the VK1 catalyst,



Scheme 2 The proposed mechanism for the dehydration reaction of sucrose to 5-HMF

was studied (Fig. 7f). It was found that there are substantial differences between DMSO and the other three solvents in both the sucrose conversion and 5-HMF yield. It has been reported that DMSO is capable of presenting catalytic activity in carbohydrates dehydration among all the high boiling points aprotic solvents [66, 67]. In the present study, the sucrose conversion and 5-HMF yield obtained > 94% and 67% in DMSO, respectively. Furthermore, the sucrose conversion of 94% and 5-HMF yield of 26% was obtained in NMP. However, when H₂O was employed as a protic solvent, no detectable HMF was observed. Besides, a mixture of THF/H₂O was used in the sucrose dehydration reaction,

which resulted in a slight increase in the 5-HMF yield to 6% at 170 °C for 1 h. The HPLC chromatogram of 5-HMF is presented in Fig. S5.

The effect of carbohydrate type

The performance of the VK1 catalyst on dehydration of different carbohydrates, including glucose, fructose and maltose, was studied under the optimum conditions. As listed in Table 3, the 5-HMF yield for fructose dehydration was obtained 68% at 170 °C for 1 h. Generally, fructose dehydration reaction is performed under milder conditions when



Fig. 7 The effect of different conditions on sucrose conversion and 5-HMF yield. Reaction conditions: **a** 200 mg sucrose, 4 ml DMSO, 10 mg catalyst, time: 30 min, temperature: 130 °C; **b** 200 mg sucrose, 4 ml DMSO, catalyst of VK1, time: 30 min, temperature: 130 °C; **c** 200 mg sucrose, 4 ml DMSO, 10 mg catalyst of VK1, time: 30 min;

d 200 mg sucrose, 4 ml DMSO, 10 mg catalyst of VK1, temperature: 170 °C; **e** 4 ml DMSO, 10 mg catalyst of VK1, temperature: 170 °C, time: 60 min; and **f** 250 mg sucrose, 4 ml solvent, 10 mg catalyst of VK1, temperature: 170 °C, time: 60 min. RSD: 5-HMF<7%, sucrose <8%

 Table 3
 The catalytic activity of the VK1 catalyst on dehydration of other carbohydrates

Carbohydrate	5-HMF yield (%)	Carbohydrate conversion (%)		
Fructose	68	100		
Glucose	33	94		
Maltose	20	91		
Maltose*	43	98		

Conditions: Carbohydrate: 250 mg, VK1 catalyst: 10 mg, Solvent: 4 mL DMSO, Temperature: 170 °C, Time: 60 min, *Time: 150 min. RSD: 5-HMF < 6%, carbohydrates < 8%

compared to glucose and maltose, which is comprised of two glucose monomers.

The catalyst reusability

Four consecutive dehydration reactions were performed under the optimized conditions to evaluate the reusability of the VK1 catalyst, as depicted in Fig. 8. After the accomplishment of each dehydration reaction, VK1 was separated by using centrifugation, followed by washing with acetone



Fig. 8 Reusability efficiency of the VK1 catalyst. Conditions: sucrose: 250 mg, VK1 catalyst: 10 mg, Solvent: 4 mL DMSO, temperature: 170 °C, time: 60 min. RSD: 5-HMF < 7%, sucrose < 3%

and drying at 120 °C overnight before being utilized for the next run. It should be noted that no considerable change

Table 4Comparison betweenthe performance of the VK1catalyst and some catalystsof previous studies in sucrosedehydration

Entry	Catalyst	T (°C)	Time (h)	Solvent	5-HMF yield (%)	Reference
1	Nb ₅ W ₅ oxide	140	2	H ₂ O/iso-butanol	46	[68]
2	Amberlite IR 120	100	15	H ₂ O	50	[69]
3	CC-SO ₃ H	130	3	[GLY(mim) ₃][Cl] ₃	77	[70]
4	ZnCl ₂	189	1	H ₂ O	57.7	[71]
5	VK1	165	1	DMSO	67	This work

was observed in both the 5-HMF yield and the sucrose conversion.

The analysis of the recycled VK1 catalyst was conducted by using FT-IR and XRD analyses. It is obvious in Fig. S1 that there are no additional bands in the FT-IR spectrum of the recycled catalyst. According to Fig. S6, the retained phase of VOHPO₄.0.5H₂O can be confirmed through the wide-angle XRD pattern of the reused VK1. In both analyses, the intensity of the peaks decreased compared to the fresh one indicating some VHP leaching during the reaction.

Comparison to previous reports

For better evaluation of the present catalytic system efficiency, a comparison was drawn with the same systems having been reported in the literature, as presented in Table 4. The 5-HMF yield in the present research was appreciably higher than the one provided by using the acidic ion exchange resin Amberlite IR 120 or Nb-W Oxide (entries 1, 2) and only slightly lower than the one provided by using CC-SO₃H and ionic liquid, (entries 3), in which the ionic liquids were prepared by costly multi-step synthesis routes. The results obtained in our study were much better than those provided by utilizing $ZnCl_2$ as a homogenous catalyst at much higher temperatures (entries 4).

Conclusion

In summary, the impregnation method was used for the preparation of VHP/KIT-6 catalysts. Unsupported VHP and VPP phases were also prepared in comparison with supported VHP. Also, calcined VPO was prepared to compare with uncalcined VPO in terms of catalytic activity. The prepared samples were utilized to investigate their catalytic activity in the sucrose dehydration reaction. It was demonstrated that the structure of mesoporous cubic silica KIT-6 could be retained after the loading of VHP on the support. Moreover, through dispersing the VHP phase on the KIT-6 support, the specific surface area, surface acidity, and catalytic activity of the catalysts were affected. As a result of preventing the unwanted rehydration and polymerization, the VK1 catalyst possessing higher surface area and lower surface acidity could provide much better catalytic activity.

Besides, the effect of different parameters on the dehydration reaction was studied in this work to achieve a better sucrose conversion and a superior 5-HMF yield. Based on the obtained results, it was concluded that the VHP loading value and solvent type played an essential role in the reaction because of the surface acidity value and catalytic activity of DMSO in dehydration reaction, respectively. Besides, not only the outstanding catalytic activity in dehydration of sucrose and other carbohydrates but also simply recycling the catalysts indicated their ability to produce value-added materials.

Supplementary Information The online version of this article (https://doi.org/10.1007/s13738-021-02191-2) contains supplementary material, which is available to authorized users.

Acknowledgments The authors would like to thank the financial supports from the Isfahan University of Technology for this work (Research Council Grant).

References

- L.T. Mika, E. Csefalvay, A. Nemeth, Chem. Rev. 118, 505–613 (2017)
- A.N. Chermahini, M. Assar, J. Iran. Chem. Soc. 16, 2045–2053 (2019)
- Z. Babaei, A.N. Chermahini, M. Dinari, M. Saraji, A. Shahvar, Sustain. Energ. Fuels 3, 1024–1032 (2019)
- A. Maleki, A.A. Jafari, S. Yousefi, Carbohydr. Polym. 175, 409– 416 (2017)
- A. Maleki, H. Movahed, P. Ravaghi, Carbohydr. Polym. 156, 259–267 (2017)
- A. Maleki, V. Eskandarpour, J. Iran. Chem. Soc. 16, 1459–1472 (2019)
- 7. J.J. Bozell, G.R. Petersen, Green Chem. 12, 539–554 (2010)
- U.M. Shapla, M. Solayman, N. Alam, M.I. Khalil, S.H. Gan, Chem. Cent. J. 12, 35–53 (2018)
- M. Murkovic, M.A. Bornik, Mol. Nutr. Food Res. 51, 390–394 (2007)
- Z. Li, Y. Yuan, Y. Yao, X. Wei, T. Yue, J. Meng, Food Control 102, 56–68 (2019)
- A.F. Sousa, C. Vilela, A.C. Fonseca, M. Matos, C.S. Freire, G.J.M. Gruter, J.F. Coelho, A.J. Silvestre, Polym. Chem. 6, 5961–5983 (2015)
- 12. A. Jain, S.C. Jonnalagadda, K.V. Ramanujachary, A. Mugweru, Catal. Commun. 58, 179–182 (2015)

- 13. Z. Zhang, G.W. Huber, Chem. Soc. Rev. 47, 1351–1390 (2018)
- F.J. Santiago-Medina, A. Pizzi, S. Abdalla, J. Renew. Mater. 5, 1–13 (2017). https://doi.org/10.7569/JRM.2017.634166
- 15. Z. Yuan, Y. Zhang, C. Xu, RSC adv. 4, 31829–31835 (2014)
- Z. Zhao, S. Sun, D. Wu, M. Zhang, C. Huang, K. Umemura, Q. Yong, Polymers 11, 1909–1924 (2019)
- 17. S.M. Basha, J. Agr. Food Chem. 40, 780-783 (1992)
- A. Jain, A.M. Shore, S.C. Jonnalagadda, K.V. Ramanujachary, A. Mugweru, Appl. Catal. A Gen. 489, 72–76 (2015)
- S. Marullo, C. Rizzo, A. Meli, F. D'Anna, A.C.S. Sustain, Chem. Eng. 7, 5818–5826 (2019)
- X. Li, Y. Wang, X. Xie, C. Huang, S. Yang, RSC adv. 9, 9041– 9048 (2019)
- T. Deng, X. Cui, Y. Qi, Y. Wang, X. Hou, Y. Zhu, ChemComm 48, 5494–5496 (2012)
- V. Choudhary, S.H. Mushrif, C. Ho, A. Anderko, V. Nikolakis, N.S. Marinkovic, A.I. Frenkel, S.I. Sandler, D.G. Vlachos, J. Am. Chem. Soc. 135, 3997–4006 (2013)
- 23. J.Y.G. Chan, Y. Zhang, Chemsuschem 2, 731-734 (2009)
- 24. W. Kunz, K. Häckl, Chem. Phys. Lett. 661, 6-12 (2016)
- M. Rezaei, A.N. Chermahini, H.A. Dabbagh, Chem. Eng. J. 314, 515–525 (2017)
- M. Rezaei, A.N. Chermahini, H.A. Dabbagh, J. Environ. Chem. Eng. 5, 3529–3539 (2017)
- A. Moslemi, A.N. Chermahini, J.N. Sarpiri, S. Rezaei, M. Barati, J. Taiwan Inst. Chem. E. 97, 237–246 (2019)
- 28. K. Parida, G.C. Behera, Catal. Lett. 140, 197-204 (2010)
- 29. F. Wang, J.L. Dubois, W. Ueda, Appl. Catal. A Gen. **376**, 25–32 (2010)
- N.P. Rajan, G.S. Rao, V. Pavankumar, K.V. Chary, Catal Sci. Technol. 4, 81–92 (2014)
- C. Tian, X. Zhu, S.H. Chai, Z. Wu, A. Binder, S. Brown, L. Li, H. Luo, Y. Guo, S. Dai, Chemsuschem 7, 1703–1709 (2014)
- C. Carlini, P. Patrono, A.M.R. Galletti, G. Sbrana, Appl. Catal. A Gen. 275, 111–118 (2004)
- 33. G.C. Behera, K. Parida, Catal Sci. Technol. 3, 3278–3285 (2013)
- J.N. Sarpiri, A.N. Chermahini, M. Saraji, A. Shahvar, Renew. Energy 164, 11–22 (2020)
- I. Sádaba, S. Lima, A.A. Valente, M.L. Granados, Carbohydr. Res. 346, 2785–2791 (2011)
- 36. F. Wang, J.L. Dubois, W. Ueda, J. Catal. 268, 260–267 (2009)
- Y. Kamiya, H. Nishiyama, M. Yashiro, A. Satsuma, T. Hattori, J. Jpn. Pet. Inst. 46, 62–68 (2003)
- X. Feng, Y. Yao, Q. Su, L. Zhao, W. Jiang, W. Ji, C.T. Au, Appl. Catal. B- Environ. 164, 31–39 (2015)
- E. Doustkhah, J. Lin, S. Rostamnia, C. Len, R. Luque, X. Luo, Y. Bando, K.C.W. Wu, J. Kim, Y. Yamauchi, Chem. Eur. J. 25, 1614–1635 (2019)
- 40. S. Rostamnia, E. Doustkhah, RSC Adv. 4, 28238–28248 (2014)
- B. Karimi, M. Vafaeezadeh, ChemComm 48, 3327–3329 (2012)
 A. Maleki, Z. Hajizadeh, R. Firouzi-Haji, Microporous Mesoporous Mater. 259, 46–53 (2018)
- A. Maleki, A.A. Jafari, S. Yousefi, J. Iran. Chem. Soc. 14, 1801– 1813 (2017)

- Z. Mohammadbagheri, A.N. Chermahini, J. Ind. Eng. Chem. 62, 401–408 (2018)
- M.M. Tabrizi, A.N. Chermahini, Z. Mohammadbagheri, J. Environ. Chem. Eng. 7, 103420–103426 (2019)
- B. Karimi, S. Abedi, J.H. Clark, V. Budarin, Angew. Chem. Int. Ed. 45, 4776–4779 (2006)
- L. Qian, Y. Ren, T. Liu, D. Pan, H. Wang, G. Chen, Chem. Eng. J. 213, 186–194 (2012)
- B. Dou, Q. Hu, J. Li, S. Qiao, Z. Hao, J. Hazard. Mater. 186, 1615–1624 (2011)
- A. Boulaoued, I. Fechete, B. Donnio, M. Bernard, P. Turek, F. Garin, Microporous Mesoporous Mater. 155, 131–142 (2012)
- L. Kumaresan, A. Prabhu, M. Palanichamy, V. Murugesan, J. Taiwan Inst. Chem. E. 41, 670–675 (2010)
- M. Falahati, L. Ma'mani, A.A. Saboury, A. Shafiee, A. Foroumadi, A.R. Badiei, Biochim. Biophys. Acta 1814, 1195–1202 (2011)
- G. Karthikeyan, A. Pandurangan, J. Mol. Catal. A Chem. 58, 361–362 (2012)
- 53. F. Kleitz, S.H. Choi, R. Ryoo, Chem Comm, 2136–2137 (2003)
- 54. W. Ji, L. Xu, X. Wang, Z. Hu, Q. Yan, Y. Chen, Catal. Today 74, 101–110 (2002)
- B. Hu, H. Liu, K. Tao, C. Xiong, S. Zhou, J. Phys. Chem. C 117, 26385–26395 (2013)
- 56. N. Mizuno, H. Hatayama, M. Misono, Chem. Mater. 9, 2697–2698 (1997)
- 57. D.B. Asay, S.H. Kim, J. Phys. Chem. B 109, 16760-16763 (2005)
- Z. Luan, M. Hartmann, D. Zhao, W. Zhou, L. Kevan, Chem. Mater. 11, 1621–1627 (1999)
- T. Okuhara, N. Ryumon, N. Yamamoto, N. Hiyoshi, Stud. Surf. Sci. Catal. 145, 271–274 (2003)
- 60. G. Dong, L. Zhang, J. Mater. Chem. 22, 1160-1166 (2012)
- C.J. Kiely, A. Burrows, S. Sajip, G.J. Hutchings, M.T. Sananes, A. Tuel, J.C. Volta, J. Catal. 162, 31–47 (1996)
- H. Jadhav, C.M. Pedersen, T. Sølling, M. Bols, Chemsuschem 4, 1049–1051 (2011)
- H. Zhao, J.E. Holladay, H. Brown, Z.C. Zhang, Science 316, 1597–1600 (2007)
- Y.J. Pagan-Torres, T. Wang, J.M.R. Gallo, B.H. Shanks, J.A. Dumesic, Acs Catal. 2, 930–934 (2012)
- F. Salak Asghari, H. Yoshida, Ind. Eng. Chem. Res. 45, 2163– 2173 (2006)
- A.S. Amarasekara, L.D. Williams, C.C. Ebede, Carbohydr. Res. 343, 3021–3024 (2008)
- 67. F. Delbecq, C. Len, Molecules 23, 1973-1989 (2018)
- B. Guo, L. Ye, G. Tang, L. Zhang, B. Yue, S.C.E. Tsang, H. He, Chin. J. Chem. 35, 1529–1539 (2017)
- J. Pérez-Maqueda, I. Arenas-Ligioiz, Ó. López, J.G. Fernández-Bolaños, Chem. Eng. Sci. 109, 244–250 (2014)
- P.V. Rathod, R.B. Mujmule, W.J. Chung, A.R. Jadhav, H. Kim, Catal. Lett. 149, 672–678 (2019)
- B. Zheng, Z. Fang, J. Cheng, Y. Jiang, Z. Naturforsch, B 65, 168– 172 (2010)