



Catalytic conversion of glucose to small polyols over a binary catalyst of vanadium modified beta zeolite and Ru/C

Joby Sebastian, Mingyuan Zheng*, Xinsheng Li, Jifeng Pang, Chan Wang, Tao Zhang

Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning, China

ARTICLE INFO

Article history:

Received 29 May 2018

Revised 14 August 2018

Accepted 3 October 2018

Available online 18 October 2018

Keywords:

Vanadium

Glucose

Retro-aldol condensation

Polyols

Hydroxyacetone

ABSTRACT

Catalytic conversion of glucose, the most abundant carbohydrate, to chemicals of petroleum origin has great desirability in terms of sustainability and industrial implementation. In this work, we attempted to exploit the vanadium-based catalysts with high retro-aldol condensation (RAC) activity for the synthesis of small polyols from glucose. Vanadium species incorporated or anchored beta zeolites were found to work effectively in synergy with 1Ru/AC to produce hydroxyacetone (HA) as the major product (34%) in a semi-continuously stirred tank reactor under 5% glucose concentration. Catalyst characterization by UV-vis and Raman spectral analysis revealed vanadium species mainly stayed in the incorporated form (tetrahedral) at 0.5% of loading and in the supported form (octahedral) at higher loadings up to 8%. Pyridine infrared spectra and temperature programmed desorption of NH₃ revealed weak Lewis acid sites in dominance. Vanadium species in the catalysts displayed multiple catalytic roles (isomerization and RAC reaction, and synergism with the hydrogenation catalyst) in the synthesis of HA from glucose. Structure-activity correlation pointed out that the catalytic activity of vanadium species is not dependent on its coordination status, nevertheless, the adjacent vanadium atoms could possibly improve the isomerization rate over the RAC rate in favor of high yield of HA. The catalyst system is recyclable to at least five times without any considerable loss in its activity and structural integrity. The results presented here provide a promising route for the sustainable production of HA and polyols from carbohydrates by using a highly selective vanadium catalyst.

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1. Introduction

Exploration of new and innovative pathways for the efficient conversion of biomass to various chemicals is an active area of research in the field of catalysis. Around 75% of the plant biomass is constituted by carbohydrates (cellulose, hemicellulose, starch and saccharides), rendering it into a sustainable platform chemical [1]. Attempts were made to synthesize diverse chemicals from carbohydrates with the assistance of catalysts. For instance, Fukuoka and co-worker first reported the direct hydrolytic conversion of microcrystalline cellulose to polyols over a recyclable 2.5%Pt/Al₂O₃ catalyst [2]. Under the optimized conditions of 190 °C and 50 bar H₂ for 24 h, 25% yield to sorbitol was achieved. In 2007, Luo et al. found that the limited accessibility of surface acid sites on Al₂O₃ could be overcome by taking advantage of the reversibly formed in situ H⁺ ions from hot water making the entire process more efficient [3]. In 2008, Zhang and co-workers reported the direct conversion of

cellulose to ethylene glycol (EG) over Ni promoted tungsten carbide catalyst [4]. Under the conditions of 245 °C and 60 bar H₂ for 0.5 h, 61% yield to EG was achieved. Quite different from the previous reports, this reaction pathway contained the breaking of C–C bond in glucose. Tungsten was identified to perform the catalytic retro-aldol condensation reaction (RAC) on glucose leading to small polyols [4b]. Thereafter, interests in small polyols from carbohydrates gained much scientific attention. This leads to the exploration of new elements capable of performing the RAC reaction and the design of new catalyst systems for new polyols [5]. In 2012, Liu et al. reported a Ru/C + 0.5%WO₃/C catalyst that could yield 1, 2-propanediol (1, 2-PD) significantly in high yields (25.7%) along with EG (37.6%) [6]. The high yield of a different polyol (C₃) however with the same element (W) performing the RAC reaction was the result of RAC reaction on fructose which was formed through the isomerization of glucose catalyzed by the carbon support. The lower rate of glucose isomerization in comparison to the RAC reaction resulted in concurrent EG production. A proper balance of isomerization, RAC reaction and hydrogenation is essential to generate high selectivity to a targeted product. Zhang and co-workers then screened various transition metal elements (Cr, Mn,

* Corresponding author.

E-mail address: myzheng@dicp.ac.cn (M. Zheng).

Fe, Co, Zn, Y, Zr, La, Ce) and non-transition elements (Al, Pb, Sn, Ba, Sr) to find an efficient element which could lead to a different polyol through isomerization/RAC reactions [7]. All the screened elements performed the isomerization/RAC reactions to a certain extent yielding EG and 1, 2-PD in varying amounts, however, some elements outperformed the others (La, Sn), yet inferior to the performance of tungsten. A very recent review by our group [8] addresses the core challenges involved in the conversion of carbohydrates to small polyols and enlists the elements reported to date for the RAC reaction. Exploration of new elements performing RAC reaction at the same time functioning in synergy with a hydrogenation catalyst, however, leading to new compounds is essential to broaden the utilization of carbohydrates.

In comparison to tungsten, vanadate ions are more effective in lowering the blood sugar level [9]. Chethana et al. carried out density functional theory (DFT) calculations to authenticate that vanadate ions are indeed more effective than tungstate and molybdate ions in glucose epimerization (involving C₂–C₃ bond rearrangement) [10]. These findings demonstrate that vanadate ions could probably act as a better RAC element than tungsten in small polyols synthesis. In 2014, Wang and co-workers reported that a homogeneous vanadyl salt, VOSO₄ can catalyze the selective transformation of glucose to lactic acid under an inert atmosphere [11]. Vanadium in the +4 oxidation state was found to be more active than that in the +5 state. Mechanistic studies revealed that lactic acid was formed by the RAC reaction of V^{IV} ions on fructose which in turn was formed by the isomerization of glucose. This confirms that the vanadyl ions can perform both isomerization and RAC reactions at temperatures as low as 150 °C. Therefore, it would be highly interesting to explore the multi catalytic behavior of vanadium in combination with a hydrogenation catalyst in the synthesis of small polyols from carbohydrates. If a proper balance between isomerization and RAC reaction and a synergy between RAC reaction and hydrogenation reaction is established, the catalyst system would outperform tungsten. Here, we explore this prospect in detail through the combination of a solid vanadium catalyst and a hydrogenation catalyst (1Ru/AC). The vanadium catalyst was designed by incorporating different amounts of vanadium into the framework of a dealuminated beta zeolite. Glucose was chosen as the reactant and the reactions were conducted in a methanol-water medium under semi-continuous mode to avoid any possible side reactions occurring during the temperature ramp. The catalysts were sensibly characterized to identify their crystalline, coordination, oxidation and acidic natures. Activity studies showed that in the absence of hydrogenation catalyst, the vanadium catalyst yield methyl lactate as the major product. However, in the presence of an optimized amount of hydrogenation catalyst, hydroxyacetone (HA) was turned out to be the major product. The catalysts worked in synergy to generate HA as the major product. We attempt here to identify and correlate the structural properties of vanadium in the synthesis of small polyols especially HA from carbohydrates. Since HA is a platform chemical [12] and the current production of which is relying on petroleum-based feedstocks [13], it is highly desirable to identify a sustainable route for its production and an efficient catalyst system for its practical application.

2. Experimental

2.1. Dealumination of beta zeolite

H-beta zeolite with Si/Al ratio of 25 (surface area = 640 m²/g, crystallinity = 95%, Na₂O = 0.05%) was supplied by Nankai University. Aluminium leaching was performed in 65% HNO₃ (10 mL/g of catalyst) at 80 °C for 12 h. Afterwards, the solution was filtered and the precipitate was washed with copious amount of deionized wa-

ter until pH became neutral. It was then dried at 80 °C overnight and finally calcined at 550 °C for 6 h.

2.2. Incorporation of vanadium

Vanadium incorporation was performed according to the wet impregnation method. VCl₃ (Alfa Aesar) was dissolved in absolute ethanol, to which dealuminated zeolite was added and stirred for 2 h. The solvent was then evaporated off at 80 °C in a temperature controlled oven and maintained at the same temperature overnight. It was then ground and calcined at 600 °C for 3 h. Here onwards, the samples are denoted as xV/HB-deAl where x denotes the weight percentage of vanadium.

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns of the catalysts were recorded in the 2θ range of 5°–60° on a PANalytical X'Pert PRO diffractometer equipped with a Cu Kα radiation source (λ = 0.15432 nm, 40 kV and 40 mA) and a proportional counter detector. UV-vis spectra of the samples were collected on a PerkinElmer Lambda 950 spectrometer in transmittance mode from 200–800 nm. The type of acid sites on xV/HB-deAl was identified by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy of adsorbed pyridine (Bruker Tensor 27, resolution = 4 cm⁻¹) and their total amount was calculated by temperature programmed ammonia desorption (NH₃-TPD) technique (Micrometrics AutoChem II). Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to analyze (Perkin-Elmer Optima 7300DV) the elemental composition of the catalysts.

2.4. Reaction procedure

The catalytic reactions were performed in a high-pressure Parr-4848 Hastelloy autoclave (100 mL) equipped with a mechanical stirrer and an automatic temperature control system. A volume of 45 mL of anhydrous methanol was charged into the reactor along with xV/HB-deAl and 1Ru/AC (supplied by Rui Ke New Materials Limited Company, type R₁S₁, 1%Ru, mesh size 250–300) catalysts. The reactor was initially purged 5 times with hydrogen and then pressurized to 30 bar. When the reactor temperature reached the set temperature of 220 °C (4 °C/min), the aqueous glucose solution (5 mL, so as to make a final concentration of glucose in the reactor of 1% or 5%) was fed into the reactor using an HPLC pump (1 mL/min). After the feeding, the reaction was allowed to continue for 0.5 h. At the end of the reaction time, the reactor was immediately cooled down to room temperature using a water bath. The reaction products were analyzed with a GC-MS instrument equipped with a Carbowax column and quantified by an HPLC (conditions: 45 °C, H₂O as the mobile phase at 0.5 mL/min) and a GC (FFAP column, FID detector) instruments using benzyl alcohol as the internal standard. The recycle experiments were conducted as follows; after the reaction, the catalysts were recovered by centrifugation, washed several times with anhydrous methanol and dried at 80 °C overnight. They were then used for the next run without any further pretreatments.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 displays the XRD patterns of beta zeolites before dealumination, after dealumination and after V incorporation procedures. All the materials after post treatments showed a pattern similar to the parent H-beta designating that the dealumination and the V incorporation procedures did not largely destroy the crystallinity

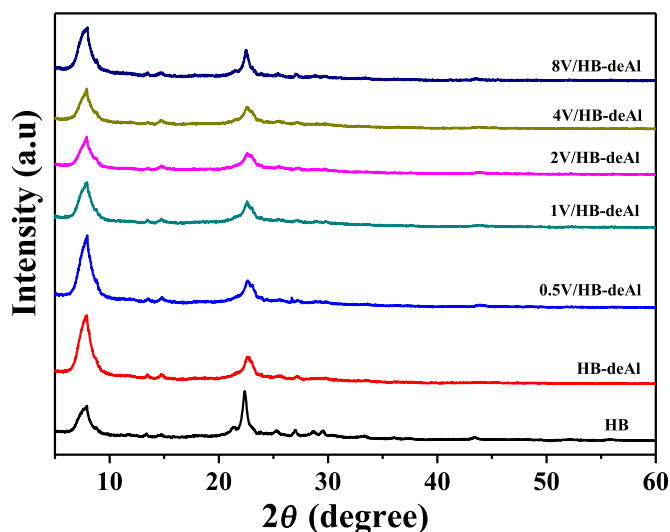


Fig. 1. XRD patterns of HB, HB-deAl and xV/HB-deAl catalysts.

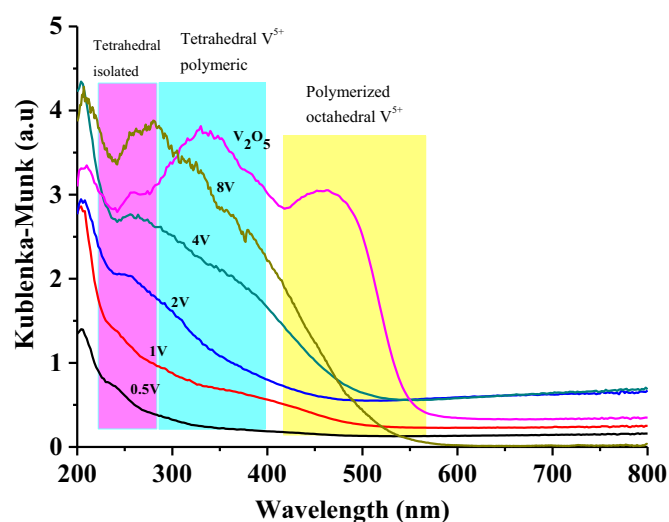


Fig. 2. UV-vis spectra of xV/HB-deAl catalysts.

and the structural integrity of the zeolite. No additional peaks due to V_2O_5 crystallites or impurities were observed in the XRD patterns. Generally, the diffraction peak at 22° – 23° is scrutinized to check the lattice contraction/expansion in beta zeolites as a result of removal/incorporation of Al/foreign elements [14]. The parent H-beta zeolite of the present study has a d_{302} spacing of 3.9296 Å. This d-spacing decreased to 3.8783 Å after dealumination due to lattice contraction caused by the removal of Al (the average Al-O bond length is longer than Si-O bond length) [15]. Since the covalent radii of V are larger than Si, a slight increment in the d_{302} spacing is anticipated if V is incorporated into the framework. The d_{302} spacing of xV/HB-deAl catalysts gradually increased with increase in V content indicating that at least a fraction of V is successfully incorporated into the zeolite framework. The d_{302} spacing of 0.5V, 2V, 4V and 8V/HB-deAl are 3.8817, 3.8953, 3.9038 and 3.9089 Å respectively and falls within the range reported in the literature [14b]. Based on ICP analysis, the Al content in the parent HB zeolite was estimated to be 3.9 wt%. After dealumination, it decreased to 0.195 wt%. The vanadium content in xV/HB-deAl catalysts did not vary much from their input values except for 8V/HB-deAl. The output vanadium content in (0.5, 1, 2, 4 and 8)V/HB-deAl catalysts were 0.52, 0.95, 1.82, 3.7 and 7.2 wt% respectively. Although theoretically, a vanadium content of only above 7.4 wt% would be in the supported form, considering the difficulty of incorporating a large amount of V in the zeolite through post-synthesis method, we expect that most of the V would be in the supported form anchored to the surface through the V-O-support bond.

The oxidation state and the coordination environment of V in xV/HB-deAl catalysts were examined by UV-vis spectroscopy. Fig. 2 shows the UV-vis spectra of all catalysts along with V_2O_5 for comparison. The absence of d-d bands in the range of 600–800 nm confirms the absence of V^{IV} ($3d^1$) ions in the catalysts. Bands in the range of 220–280 nm correspond to isolated V^V species in tetrahedral coordination (monomeric vanadyl species, $(-\text{SiO})_3\text{V}=\text{O}$). Bands in the range of 285–395 nm are also assignable to V^V species in tetrahedral coordination but in a polymeric state ($(-\text{SiO})(\text{V}-\text{O}-\text{V})_2\text{V}=\text{O}$). Bands ranging from 420 to 565 nm indicates the presence of polymerized V^V species in octahedral coordination (VO_6 units) [14b,16,17]. Octahedral vanadium species implies vanadium in the supported state as V_2O_5 . The absence of XRD peaks corresponding to V_2O_5 in Fig. 1 indicates their high dispersion or amorphous nature. 0.5V/HB-deAl showed bands mainly due to

isolated V^V species in tetrahedral coordination with very little or negligible contribution from polymerized tetrahedral species. As the amount of V in the catalysts was increased, the V^V species in polymerized state emerged and increased. 8V/HB-deAl catalyst possessed the maximum contribution of polymerized V^V species in both tetrahedral and octahedral coordination. These observations were further confirmed by the Raman spectral analysis recorded at two different laser wavelengths of 325 nm and 532 nm corresponding to UV and visible regions to identify the monovanadyl and polyvanadyl species respectively (Supplementary information S1).

The nature of acid sites on xV/HB-deAl catalysts was identified by the analysis of FTIR spectroscopy of adsorbed pyridine. Fig. 3 shows the representative spectra of some of the catalysts. The room temperature spectra of HB-deAl showed bands only due to Lewis acid sites demonstrating the removal of Al from the lattice sites during the dealumination procedure. When 0.5 wt% of V was incorporated into the framework of HB-deAl, a spectrum similar to HB-deAl was observed, indicating that V incorporation did not generate Brønsted acidity in the catalyst. All the bands due to Lewis acid sites vanished when the temperature of desorption was raised to 150 °C specifying their weak nature. Once the V content was increased to 8 wt%, an additional weak band at 1545 cm^{-1} representing Brønsted acidity was observed. This could possibly due to the hydrolysis of $(\text{Si}-\text{O})_3\text{V}=\text{O}$ species to $(\text{Si}-\text{O})_2\text{V}=\text{O}$ (OH) species when exposed to air [16]. Although weakly existed at 250 °C, all these bands completely vanished at 350 °C. In contrast, V incorporated on the parent HB zeolite displayed prominent bands due to Lewis and Brønsted acid sites even at a desorption temperature of 350 °C portraying their inherent strong acidic nature. The total amount of acid sites in the catalysts was quantified using the NH_3 -TPD technique. Fig. 4 shows the NH_3 -TPD profiles of representative catalysts. 4V/HB-deAl and 8V/HB-deAl showed a single, slightly broad peak (indicative of different strength distributions) centred at 160 °C. The peak position designates the weak nature of acid sites confirming the inferences made in the Py-IR spectral analysis. These desorption peaks were virtually non-existent in the case of HB-deAl, 0.5V/HB-deAl and 1V/HB-deAl catalysts. Although the catalysts are comprised of different acid sites of slightly different strengths, their total acidity followed a linear trend as 8V/HB-deAl ($298\ \mu\text{mol/g}$) > 4V/HB-deAl ($180\ \mu\text{mol/g}$) > 1V/HB-deAl ($43\ \mu\text{mol/g}$) > 0.5V/HB-deAl ($25\ \mu\text{mol/g}$) (Supplementary information S2).

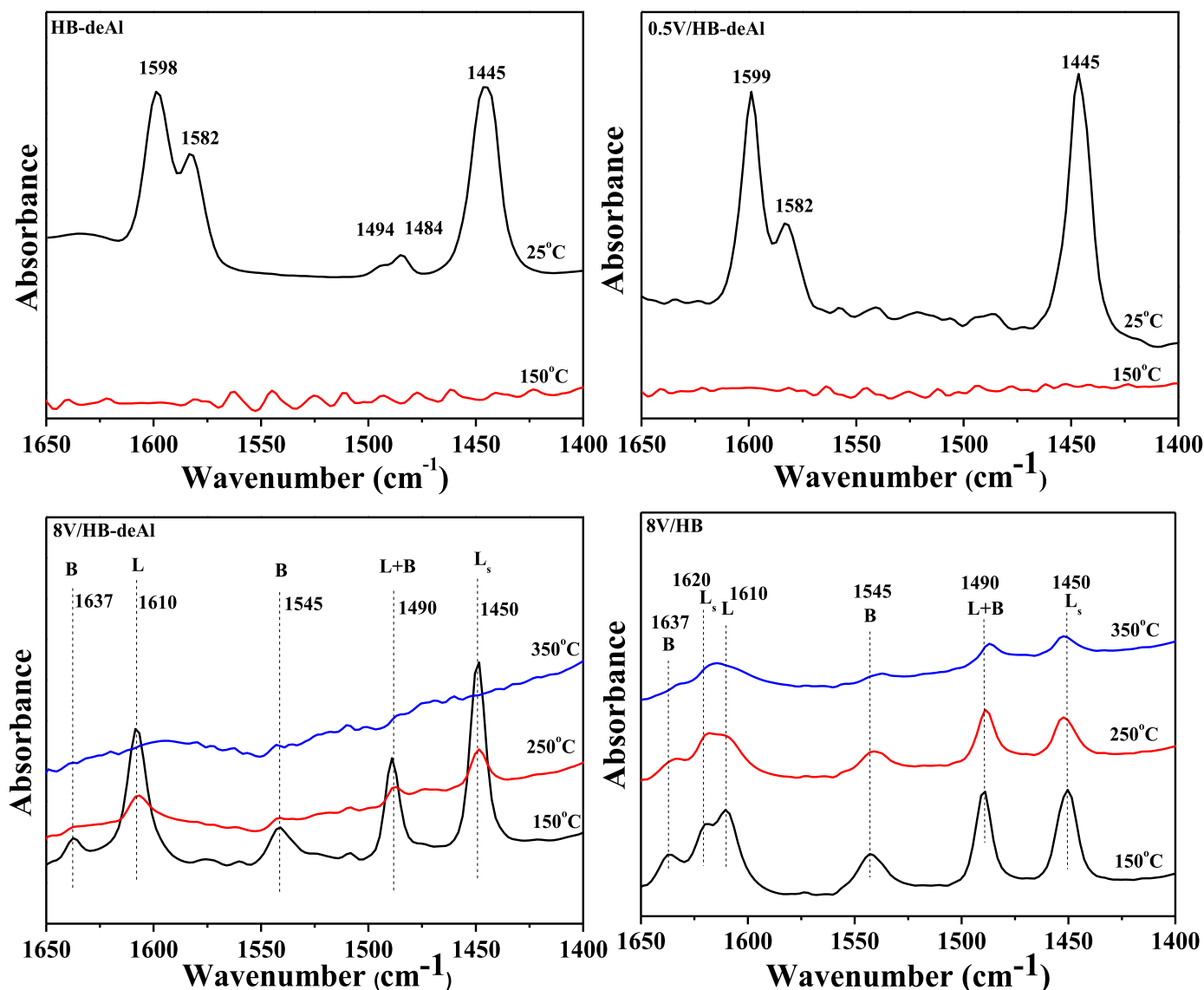


Fig. 3. Py-IR spectra of HB-deAl, 0.5 V/HB-deAl, 8 V/HB-deAl and 8 V/HB catalysts.

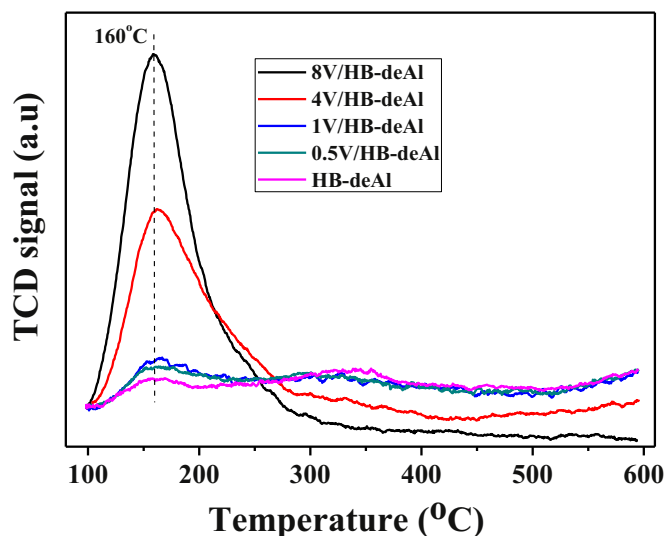


Fig. 4. NH_3 -TPD profiles of HB-deAl, 0.5 V/HB-deAl, 1 V/HB-deAl, 4 V/HB-deAl and 8 V/HB-deAl catalysts.

3.2. Catalytic activity

Table 1 summarizes the catalytic performance of various vanadium compounds (VOSO_4 , NH_4VO_3 , V_2O_5 and 4V/HB-deAl) in combination with 1Ru/AC in the conversion of 1% glucose solution. All the vanadium catalysts were active for the RAC reaction. The quantified products include HA, methyl lactate (MLA), 1-hydroxybutan-2-one (HB), methyl glycolate (MG), glycolaldehyde dimethylacetal (GDA), 3-hydroxybutan-2-one (acetoin), EG, 1,2-PD and sorbitol. The catalysts also produced some minor compounds like 2,5-dimethyl furan, acetic acid-dimethoxy methyl ester, 2-hydroxy-3-pentanone, acetic acid hydroxy methylester, etc., which were not quantified due to their less contribution by the best performance catalyst. Supplementary information S3 and S4 provide the GC-MS spectra of the product mixture of V_2O_5 and 4V/HB-deAl catalysts respectively. The major compounds produced by vanadium species in the +5 oxidation state (NH_4VO_3 , V_2O_5 and 4V/HB-deAl) were HA and MLA. Vanadium in the +4 oxidation state was found to be inferior in activity. Wang and co-workers [11] reported that under an inert atmosphere of N_2 , V in the +4 oxidation state was more active in lactic acid synthesis than the +5 oxidation state. However, in the present scenario, the +5

Table 1. Catalytic performance of various vanadium compounds in the synthesis of small polyols from glucose.

Catalyst	Product distribution (% C yield)									
	HA	MLA	HB	MG	GDA	Acetoin	Sorb.	EG	1,2-PD	Total
4V/HB-deAl	23.0	21.1	5.1	1.4	6.6	3.0	3.7	7.0	3.7	74.6
V ₂ O ₅	21.4	18.8	4.0	–	9.2	–	3.4	6.7	5.1	76.8
NH ₄ VO ₃	27.3	10.1	4.5	1.5	4.8	3.9	2.6	2.4	3.1	60.2
VOSO ₄	6.8	11.2	2.9	1.5	4.3	1.0	2.7	4.5	–	35.1

Reaction conditions: $V = 0.118$ mmol, $1\text{Ru}/\text{AC} = 0.025$ g, $\text{glucose}_{\text{aq}} = 5$ mL (feeding rate = 1 mL/min), $\text{MeOH} = 45$ mL, $T = 220$ °C, $P_{\text{H}_2} = 30$ bar, reaction time after feeding = 30 min. Concentration of glucose in the reactor is 1%.

Table 2. Catalytic performance of $x\text{V}/\text{HB-deAl}$ catalysts under 5% glucose solution.

Catalyst	Product distribution (% C yield)									
	HA	MLA	HB	GDA	MG	Acetoin	Sorb.	EG	1,2-PD	Total
0.5V/HB-deAl	18.2	2.6	4.5	0.5	0.22	3.2	0.05	0.95	0.59	30.9
1V/HB-deAl	22.3	2.1	5.5	1.6	0.31	4.1	0.36	2.14	1.3	39.7
2V/HB-deAl	26.5	2.1	6.3	2.1	0.29	5.2	0.72	3.8	1.9	49.0
4V/HB-deAl	29.2	2.3	7.0	3.1	0.24	6.0	1.1	3.5	2.0	54.1
8V/HB-deAl	34.3	5.8	6.6	6.0	0.17	4.9	5.2	4.1	1.9	69.1
1Ru/AC ^a	9.4	0.43	2.4	2.0	0.15	0.57	14.3	5.6	3.3	38.1
4V/HB-deAl ^b	4.0	27.2	3.2	3.4	2.3	1.4	3.5	6.3	5.3	57.8
HB-deAl ^c	7.1	0.45	1.9	0.74	–	–	17.0	1.8	1.1	30.1

Reaction conditions: $V = 0.235$ mmol, $1\text{Ru}/\text{AC} = 0.30$ g, $\text{glucose}_{\text{aq}} = 5$ mL (feeding rate = 1 mL/min), $\text{MeOH} = 45$ mL, $T = 220$ °C, $P_{\text{H}_2} = 30$ bar, reaction time after feeding = 0.5 h. Concentration of glucose in the reactor is 5%.

^a Without V and 2,5-hexanedione was found in 9.7%.

^b Without 1Ru/AC.

^c Equivalent to the amount of HB-deAl in 0.5V/HB-deAl.

oxidation state outperformed the +4 oxidation state even in producing MLA (Table 1), an esterified form of lactic acid. Comparing the catalytic performance of various vanadium compounds in +5 state, it is clear from Table 1 that the homogeneous NH₄VO₃ is the most active in producing HA in a yield of 27% contributing to a total carbon balance of quantified products to 60%. Although the HA yield of V₂O₅ and 4V/HB-deAl was little lower than NH₄VO₃ (21.4% and 23% respectively), their combined yield of HA and MLA, and the total yield of quantified products were significantly higher than NH₄VO₃ (76.8% and 74.6%, respectively). Considering the water solubility of V₂O₅ where the majority of the catalytic activity would be generated by homogeneous V^V ions, 4V/HB-deAl turned out to be a suitable representative solid catalyst for exploring the RAC reaction of glucose to small polyols.

A catalyst system is industrially more attractive if it could display a similar performance under high reactant concentration. Table 2 shows the catalytic performances of $x\text{V}/\text{HB-deAl}$ ($x = 0.5, 1, 2, 4,$ and 8 wt%) and HB-deAl under a glucose concentration of 5%. Except for HB-deAl, all the experiments were conducted with the same amount of vanadium (0.236 mmol) in the reaction media. First of all, it can be confirmed that vanadium species anchored on the HB-deAl played critical roles in HA formation as comparing the performance of HB-deAl and 8V/HB-deAl (7% vs 34.3%). For the vanadium modified $x\text{V}/\text{HB-deAl}$ catalysts, though at similar V content, the HA yield showed significant inconsistency. The coordination status of V in the catalysts is different (UV-vis spectra, Fig. 2). Monomeric vanadyl species dominated in 0.5V/HB-deAl. The contribution of polymeric tetrahedral and octahedral vanadyl species increased with increase in V content and reached the highest level in 8V/HB-deAl. In accordance with this trend, the HA yield showed a gradual increase with an increase in polymeric vanadyl species (18.2% to 34.3%) indicating that the catalytic activity of polymeric vanadyl species (8V/HB-deAl) are more effective than monomeric species (0.5V/HB-deAl). A plot of area percentage of monovanadyl and polyvanadyl species versus HA yield showed a linear relationship in which the HA yield increased linearly with increase in polyvanadyl species and decreased with a decrease in monovanadyl species (Supplementary information S5). As a

result of this, the total yield of quantified products increased from 30.9% over 0.5V/HB-deAl to 69.1% over 8V/HB-deAl. Nonetheless, the polymeric vanadyl species marginally increased the yields of MLA, HB, GDA, sorbitol and EG, suggesting that an optimal amount of various vanadyl species is rather important for high HA yield. Since HA is formed by the RAC reaction of vanadium species on fructose [8], this could also indicate that the polymeric vanadyl species (possibility of two or more V atoms connected to each other by O atoms) has a higher isomerization rate of glucose than monomeric vanadyl species. A proper synergy between the $x\text{V}/\text{HB-deAl}$ catalyst and the hydrogenation catalyst (1Ru/AC) is expected to generate HA as the major product. In the absence of $x\text{V}/\text{HB-deAl}$, the 1Ru/AC catalyst produced sorbitol in yield of 14.3% with 9.5% of 2,5-hexanedione as an additional compound. The low yield of sorbitol by the 1Ru/AC than reported in the literature [3,4] and the identification of new compound indicates the further consumption of sorbitol or glucose to unidentifiable products. In the absence of 1Ru/AC, the 4V/HB-deAl catalyst yielded MLA as the major product (27.2%). These experiments suggest the existence of a proper synergy between the two catalysts to generate HA. To confirm this synergism, a conditional experiment was performed as follows. At first, the reaction was conducted with 4V/HB-deAl alone which yielded 27.2% of MLA and 4.0% of HA. Afterwards 1Ru/AC was added to the reaction mixture and continued the reaction for a further half an hour. At the end of this experiment, the HA yield could not rise above 5.8% specifying that the HA formation is not consecutive (i.e., MLA hydrogenation to HA), but the result of a proper synergy between 4V/HB-deAl and 1Ru/AC catalysts (Supplementary information S6). In the absence of this synergy MLA would be generated as the main product. These experiments demonstrate the RAC ability of vanadium species working in unison with a hydrogenation catalyst to produce polyols.

In order to verify the sole effect of vanadium on the catalytic activity, not any contribution from the residual Brønsted acidity of the zeolite support, catalysts were prepared with the retention of full and some fraction of Al in the zeolite framework by adjusting the dealumination time from zero to 2 h. Brønsted acid sites either could act as synergistic promoters in the catalytic

Table 3. Effect of Al content in HB zeolite on product distribution.

Catalyst	Product distribution (% C yield)									
	HA	MLA	HB	GDA	MG	Acetoin	Sorb.	EG	1,2-PD	Total
8 V/HB-Al	16.8	2.8	4.3	1.83	0.76	2.0	0.93	4.9	3.5	37.8
8 V/HB-Al-2	22.8	2.2	5.8	3.0	0.21	4.9	1.3	4.0	2.1	46.5
8 V/HB-deAl	34.3	5.8	6.6	6.0	0.17	4.9	5.2	4.1	1.9	69.1

Reaction conditions: Catalyst = 0.150 g, 1Ru/AC = 0.30 g, glucose_{aq} = 5 mL (feeding rate = 1 mL/min), MeOH = 45 mL, T = 220 °C, P_{H₂} = 30 bar, reaction time after feeding = 0.5 h. Concentration of glucose in the reactor is 5%.

Table 4. Catalytic performance of 8V/HB-deAl under different feedstocks.

Feedstock	Product distribution (% C yield)									
	HA	MLA	HB	GDA	MG	Acetoin	Sorb.	EG	1,2-PD	Total
Glucose	34.0	5.0	6.8	7.7	0.13	3.5	4.9	6.6	1.5	69.9
Fructose	51.1	7.3	3.9	7.8	0.41	1.9	3.8 ^a	3.5	1.6	81.3
Sucrose	39.6	5.7	5.4	6.8	0.33	2.9	2.7	6.2	2.0	71.4

Reaction conditions: V = 0.235 mmol, 1Ru/AC = 0.050 g, feedstock_{aq} = 5 mL (feeding rate = 1 mL/min), MeOH = 45 mL, T = 220 °C, P_{H₂} = 30 bar, reaction time after feeding = 0.5 h. Concentration of feedstock in the reactor is 1%.

^a mannitol.

behavior of vanadium species and Ru or could promote side reactions to reduce the HA yield. Considering the strong acidic nature of Al containing beta zeolites, the latter prospect is highly expected to occur. Table 3 summarizes the catalytic performance of xV/HB catalysts containing different amount of Al. Brønsted acid sites generated by Al in the zeolite framework did not partake in synergism with the vanadium species in the catalyst and Ru to yield more HA, rather it favored more side reactions to decrease the yield of HA and the total amount of quantified products (Table 3). When Al in the parent HB was present along with 8 wt% of V, the HA yield decreased to 16.8% as compared to 34.3% in the absence of any or negligible Al. When some amount of Al was present, the yield of HA (22.8%) was in between of those with full and without Al. Supplementary information S7 provides the GC-MS spectra of the product mixture obtained over 8V/HB-Al catalyst. Brønsted acid sites have a negative impact on the catalytic performances of vanadium species and Ru, hence verifying the sole catalytic performance of vanadium species in the RAC reaction.

To check the versatility of the RAC performance of vanadium species in synergism with 1Ru/AC, different substrates such as fructose and sucrose were used as the feedstocks (Table 4). When fructose was employed as the reactant, the HA yield increased to 51.1% revealing that fructose is the reaction intermediate in the conversion of glucose to HA. With fructose, the total amount of quantified products reached > 80% depicting a good carbon balance. The decrease in HA yield when glucose was used as the feedstock point to a slow glucose to fructose isomerization rate resulting in the RAC reaction of glucose to C₂ and C₄ compounds. When a disaccharide, sucrose (glucose-fructose units) was used as the feedstock where an additional catalytic step of hydrolysis of disaccharide to monosaccharide is involved, the HA yield (39.6%) reached in between that of when the feedstocks were glucose and fructose. The weak acidity of 8V/HB-deAl could perform the hydrolysis of sucrose to glucose and fructose to a significant level demonstrating its efficient, additional catalytic role. The V/HB-deAl catalyst of present study establishes a predictable and consistent synergistic catalytic performance in the RAC reaction of monosaccharides and disaccharides to polyols. Deng et al. [18] reported the use of a 2%Ni-SnO_x/Al₂O₃ (Sn/Ni = 0.5) catalyst in the synthesis of HA from glucose and fructose with 0.4% reactant solutions in water. Glucose and fructose yielded 53% and 72.8% of HA respectively at the reaction conditions of 200 °C, 60 bar H₂ for 0.5 h in a batch process. As compared to this, the vanadium catalyst explored here shows advantages like low hydrogen pressure and a physical synergism.

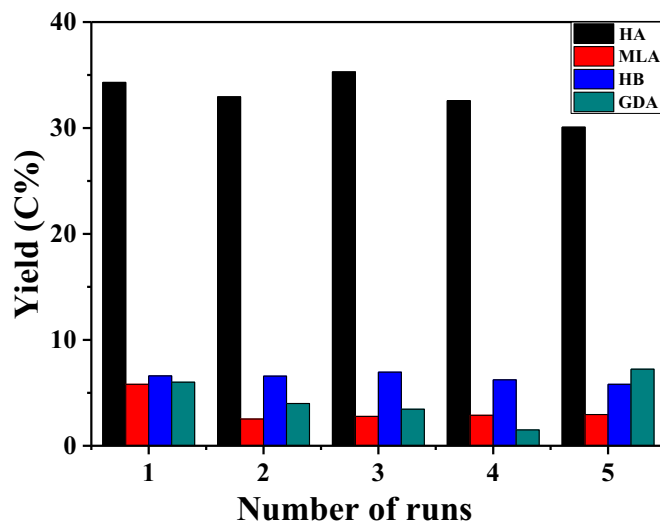
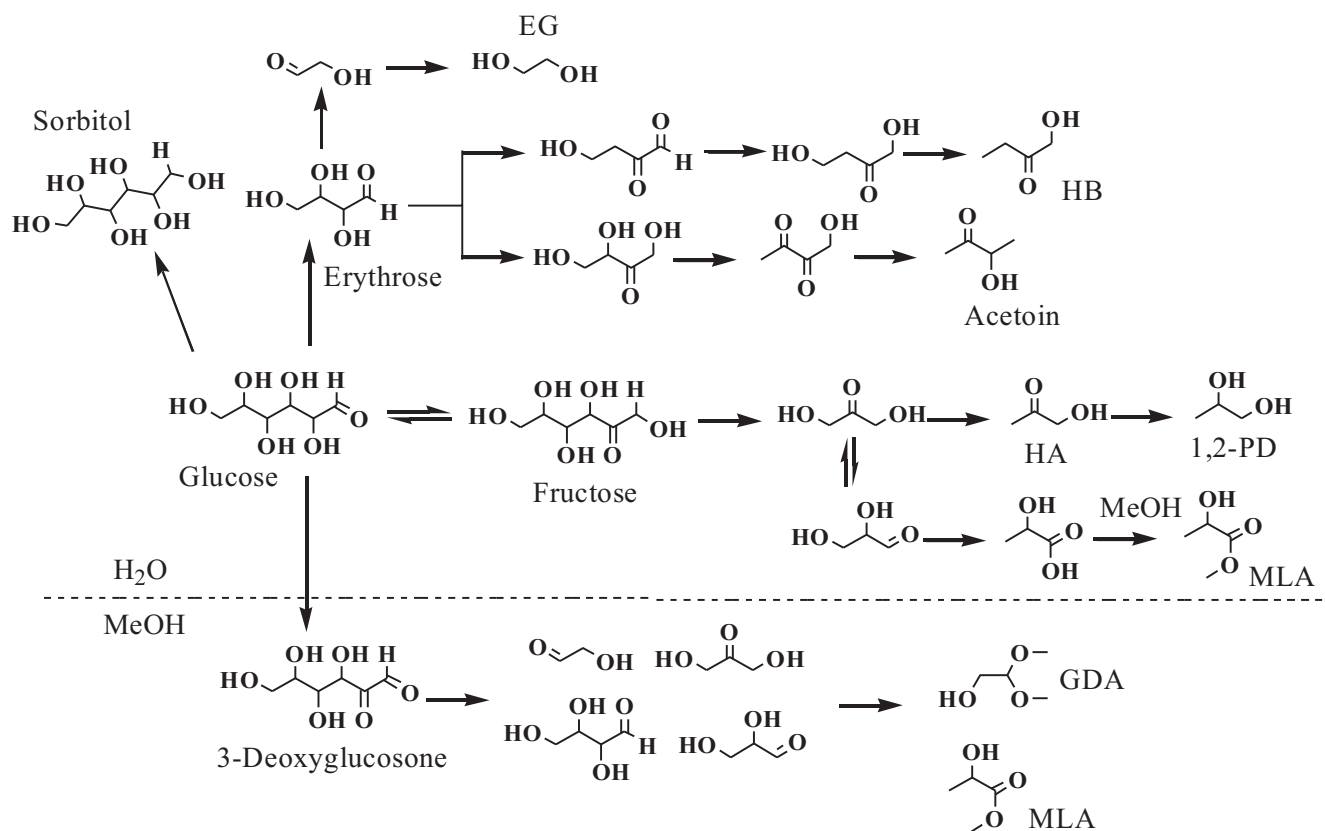


Fig. 5. Recycle runs of 8V/HB-deAl+1Ru/AC catalysts. Reaction conditions: 8V/HB = 0.15 g, 1Ru/AC = 0.30 g, glucose_{aq} = 5 mL (feeding rate = 1 mL/min), MeOH = 45 mL, T = 220 °C, P_{H₂} = 30 bar, reaction time after feeding = 0.5 h. Concentration of glucose in the reactor is 5%.

The synergistic catalyst system of the present study is stable under the reaction conditions. It could be recycled at least five times with no significant loss in its catalytic performance (Fig. 5). XRD of the catalysts after the 5th run confirmed the robust crystalline structure of the beta zeolite. Any additional peaks due to V₂O₅ crystallites or Ru nanoparticles were not detectable in the XRD demonstrating the stable nature of its active components (Supplementary information S8). The coordination environment of 8V/HB-deAl after five batch cycles of run in fresh solvents (designed to avoid the interference of residual carbon generated by 8V/HB-deAl and 1Ru/AC) was analyzed by UV-vis spectroscopy. The spectrum of the fresh catalyst and the catalyst after 5th run appeared identical (Supplementary information S9) corroborating the structural integrity of V/HB-deAl catalysts. The ICP analysis of the reaction product after a single run was performed to quantify the fractional amount of V and Ru leached into the solution. The analysis revealed 0.125% of V with respect to the amount of V taken for the reaction in the product mixture. On the other hand, ICP could not detect Ru in the product mixture. The catalytic action of solubilized V ions would be insignificant as compared to



Scheme 1. Reaction pathway for the conversion of glucose to various polyols.

the large amount of V remained in the solid catalyst, further validating the stable nature of its active components.

3.3. Reaction mechanism

Zhang and co-workers discussed a very intricate reaction mechanism incorporating all the possible intermediates and side products in the synthesis of small polyols from cellulose in water [8]. Based on this, HA could be formed by the following reaction sequence. At first, glucose undergoes isomerization to fructose, then RAC reaction to produce dihydroxyacetone which upon dehydration and hydrogenation yields HA. Hydrogenation of HA leads to 1,2-PD. Alternatively, dihydroxyacetone can undergo isomerization to form glyceraldehyde which upon dehydration, hydration and isomerization lead to lactic acid. Esterification of lactic acid with methanol leads to MLA. In parallel, glucose can also undergo RAC reaction to form erythrose and glycolaldehyde. Erythrose on RAC reaction forms glycolaldehyde and this upon hydrogenation leads to EG. HB, a precursor to 1,2-butanediol is formed from erythrose involving dehydration and hydrogenation reactions. Similarly, acetoin is also generated from erythrose through isomerization to erythrulose followed by dehydration and hydrogenation reactions. Direct hydrogenation of glucose leads to the formation of sorbitol. Apart from this reaction pathway, Taarning and co-workers proposed a comprehensive reaction scheme for the glycolytic pathway of glucose to various chemicals over Sn-containing silicates in methanol [19]. According to this, glucose first forms 3-deoxyglucosone as the central intermediate, which then undergoes RAC reaction to form C_2 - C_4 sugars and reactive aldehyde intermediates. These upon further transformation yields compounds like MLA and glycolaldehyde dimethylacetal. In addition to these compounds, many other compounds in cyclic and acyclic form could also be simultaneously generated. Based on these two reports, the

reaction products obtained over $x\text{V}/\text{HB-deAl}$ and $1\text{Ru}/\text{AC}$ in the methanol-water mixture could be a combination of both the mechanisms operating concurrently (Scheme 1). Also, a cross-over reaction pathway for any intermediate at any stage could also be possible. In essence, HA is produced by the catalytic pathway in water. In the absence of hydrogenation catalyst, dihydroxyacetone would undergo isomerization to glyceraldehyde and then to lactic acid. Lewis acidic V can then catalyze the esterification of lactic acid with methanol present in excess to yield MLA. The use of water-methanol solvent mixture enabled us to recognize the independent catalytic pathways of V to produce various polyols.

High yield of HA is achievable only under short reaction time of 0.5–1.5 h. Prolonging the reaction time up to 2 h resulted in a decrease in HA yield (Supplementary information S10), but not leading to the formation of its hydrogenated product, 1,2-PD under the present reaction conditions. To verify this, HA was taken as the reactant and the reaction was conducted for a period of 2 h, at the same time monitoring its consumption at regular time intervals (Supplementary information S11). HA consumption was 87% at the end of the 2-h reaction, but the 1,2-PD yield was only 6.8%, confirming that the further hydrogenation of HA to 1,2-PD is not effective under the reaction conditions. To identify the underlying reason behind the low hydrogenation of HA to 1,2-PD by $1\text{Ru}/\text{AC}$, an experiment was conducted by using HA as the reactant and $1\text{Ru}/\text{AC}$ as the only catalyst ($8\text{V}/\text{HB-deAl}$ was not used) under the similar reaction conditions. After a 2 h reaction, the HA conversion was 99% and surprisingly the 1,2-PD yield was 72%. These experiments confirm that the presence of vanadium species in $x\text{V}/\text{HB-deAl}$ is the critical constituent limiting the further hydrogenation of HA to 1,2-PD. Even the use of a high amount of $1\text{Ru}/\text{AC}$ along with $x\text{V}/\text{HB-deAl}$ aimed to increase the hydrogenation of HA to 1,2-PD was found to be not effective (Supplementary information S12). An increase in the hydrogenation catalyst beyond the optimum level

decreased the yield of HA. Only a particular composition of structurally distinctive xV/HB-deAl and 1Ru/AC is effective in producing a high amount of HA from carbohydrates.

4. Conclusions

The effectiveness of a vanadium catalyst in the RAC reaction of carbohydrates to small polyols was investigated. In accordance with reported experimental and theoretical studies, vanadium was found to be a good RAC element, however, lacks a proper balance of isomerization and RAC reactions. This led to an inferior performance than reported W based catalysts in terms of polyol selectivity. The vanadium catalyst works in synergy with the hydrogenation catalyst to generate polyols. If the isomerization activity/rate of the V containing catalyst is improved, it will have a great advantage over W in synthesizing C₃ polyols through multi catalytic approach. One possible reason for the low isomerization rate of vanadium species could be its low-temperature RAC activity conflicting with the low-temperature isomerization behavior. Even so, the vanadium catalyst showed promising activity in the production of commercially important HA from glucose, fructose and sucrose. HA was generated as a result of a proper synergy between the vanadium catalyst and the hydrogenation catalyst. With glucose as the substrate, an HA yield of 34.5% could be achieved over 8V/HB-deAl catalyst. When fructose was used as the feedstock, the HA yield could reach up to 51%. The catalyst system explored here is stable and could be reused up to five times without significant loss in activity. Structure-activity correlations revealed that the catalyst mainly possess weak Lewis acid sites and the catalytic function (RAC) is not related to the coordination status of vanadium. However, the HA productivity increased with increase in polymeric vanadyl species indicating that a high isomerization rate over polymeric vanadyl species than monomeric vanadyl species. This indicates that, in solid vanadium catalysts, the likelihood of adjacent vanadium atoms could possibly improve the isomerization rate over the RAC rate. We believe that upon the further improvement of catalyst design, and reaction conditions optimization, the V catalysts will perform as a better RAC element in the selective synthesis of a variety of small polyols from carbohydrates.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (nos. 21306191; 21376239; 21690080; 21690081), "Transformational Technologies for Clean Energy and Demonstration", Strategic Priority Research Program of the Chinese Academy of Sciences, Grant no. XDA 21060200. JS acknowledges DICP for the outstanding postdoc fellowship.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jchem.2018.10.003.

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