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One-pot direct conversion of levulinic acid into high-yield valeric acid over a highly stable bimetallic Nb-Cu/Zr-doped porous silica catalyst

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ABSTRACT

The direct conversion of levulinic acid (LA) to valeric biofuel is highly promising for the development of biorefineries. Herein, LA is converted into valeric acid (VA) via one-pot direct cascade conversion over non-noble metal-based Nb-doped Cu on Zr-doped porous silica (Nb-Cu/ZPS). Under mild reaction conditions (150 °C and 3.0 MPa H₂ for 4 h), LA was completely converted into VA in high yield (99.8%) in aqueous medium with a high turnover frequency of ~300 h⁻¹. The Lewis acid sites of ZPS enhanced the adsorption of LA on the catalyst surface, and both the Lewis and Brønsted acidity associated with Nb₂O₅ and the metallic Cu⁰ sites promoted catalysis of the cascade hydrogenation, ring cyclization, ring-opening, and hydrogenation reactions to produce VA from LA. The bimetallic Nb-Cu/ZPS catalyst was also effective for the conversion of VA into various valeric esters in C1–C5 alcohol media. The presence of Nb₂O₅ effectively suppressed metal leaching and coke formation, which are serious issues in the liquid-phase conversion of highly acidic LA during the reaction. The catalyst could be used for up to five consecutive cycles with marginal loss of activity, even without catalyst re-activation.

Keywords: Biofuel, Levulinic acid, Valeric acid, Valerate esters, Copper, Niobium.

1. Introduction

The chemoselective conversion of cellulose or cellulose-derived sugars into transportation fuels and value-added chemicals is one of the most promising strategies for meeting the current urgent demand for renewable and sustainable energy and chemicals.¹⁻⁴ During the last two decades, a number of different pathways for converting cellulose into value-added chemicals have been explored.^{5, 6} One of the most optimistic pathways is the conversion of C6 sugars to levulinic acid (LA) through 5hydroxymethyl furfural (5-HMF) via acid-catalyzed hydrolysis, followed by the transformation of LA to y-valerolactone (GVL) by hydrogenation, and of GVL to valeric acid (VA) by ring-opening and subsequent hydrogenation (Scheme 1).⁷⁻¹⁰ VA can then be esterified to produce valeric acid alkyl esters (VE, e.g., methyl valerate and ethyl valerate), which are recognized as a new type of cellulose-derived biofuel.^{8, 11} Other potential applications of VA include in perfumes, cosmetics, food additives, lubricants, and plasticizers, as shown in Fig. 1. Several studies have focused on the conversion of LA to GVL over noble metals on neutral supports (e.g., Ru/C and Ru/TiO₂) under relatively mild conditions (25–150 °C, 2–4.5 MPa H₂).¹²⁻¹⁴ However, the ring-opening of GVL is a highly thermodynamically unfavorable reaction that requires a large increase in the free energy ($\Delta G = +25 \text{ kJ mol}^{-1}$ in water and $\Delta G = +1.5 \text{ kJ mol}^{-1}$ in methanol).^{15, 16}

Although numerous catalysts and reaction conditions have been explored for the conversion of LA to GVL^{14, 17-21} and the conversion of GVL to VA and VE,²²⁻²⁵ the one-pot direct cascade conversion of LA to VA and VE is a more economically viable and simpler approach, because the separation and purification (which are typically high-cost, energy-intensive, and time-consuming steps) of reaction intermediates (in this case, GVL) from the unreacted feed, byproducts, and catalysts can be avoided. The direct conversion of cellulose or cellulose-derived C6/C5 sugars to LA via acid hydrolysis is could be a feasible pathway,^{7, 26} but because of the environmental pollution and low product concentration issues, hydrolysis of furfuryl alcohol is an industrially established pathway to produce LA.

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Consequently, the one-pot, direct conversion of LA to VA and VE would enable the development of a practical-scale cellulosic biofuel process. A variety of multifunctional catalysts consisting of acidic sites and metal sites and various reaction conditions (e.g., organic solvents, alcoholic solvents, and water) have been explored for this purpose (Table S1).^{21, 25, 27-35} Most previous approaches are based on the use of noble metal (Pt, Pd, or Ru) catalysts. The first example was reported by Lou *et al.*, who explored the conversion of LA to VA using 1 wt% Ru loaded on strongly acidic HZSM-5.²¹ A moderate yield of VA + VE mixtures (45.8%) was obtained at 4.0 MPa H₂ and 200 °C after 10 h of reaction in dioxane. However, the Ru/HZSM-5 catalyst was quickly deactivated due to leaching of the Ru and Al species during the conversion of highly corrosive and polar LA, thereby necessitating further work. Later, the same group examined the effects of Ru precursors, extra-framework cations (H⁺ and NH_4^+), and the Si/Al ratio in the ZSM-5 support for the conversion of LA to VA at 200 °C and 4.0 MPa H_2 in dioxane over 10 h. Increasing the number of acid sites of the zeolite support enhanced the yield of the VA + VE mixture to 91.3%; however, serious coke formation then decreased the yield of the VA + VE mixture to 66.4%, and a reactivation step was required to recover the initial activity of the catalyst.²⁷ Pan et al. developed a Brønsted acid-supported Ru-based catalyst (5 wt% Ru/SBA-SO₃H) for the conversion of LA into VA + VE;³⁵ the high VA + VE yield (94%) at 240 °C and 4 MPa H₂ after 6 h of reaction was attributed to the efficient conversion of GVL over the Brønsted acid sites. However, a significant loss of sulfur (45.7%) from the SBA-SO₃H support during LA conversion resulted in a loss of the catalyst acidity and a decrease in the yield of the VA + VE mixture. The use of non-noble metals (Ni and Cu) deposited on a SBA-SO₃H support generated the intermediate GVL as the main product. Kon et al. further studied the selective conversion of LA to VA over Pt/HMFI zeolite at 200 °C using 0.8 MPa H₂ for 6 h under solvent-free conditions, achieving a high yield of 99%.³⁴ When LA conversion was carried out in methanol at 200 °C and 0.8 MPa H₂ for 3 h, 87% methyl valerate was produced. Recently, Zhou et al. reported that the use of metal triflates as organic Lewis acids and Pd/C

resulted in a 92% VA yield at 150 °C and 5 MPa H₂ in the reaction for 6 h in *n*-octane.²⁸ However, it was difficult to recover the soluble metal triflates after completing the reaction. In addition, Pd leaching and the formation of coke on the catalyst decreased the yield of VA when the catalyst was reused. Wang *et al.* encapsulated Pd nanoparticles in the mesopores of AlMCM-41 to prepare a robust catalyst; the reaction at 270 °C and 6 MPa H₂ for 10 h in *n*-octane furnished a high LA conversion (>99%), but the VA yield was low (45%).²⁹ The Pd-encapsulated catalyst showed marginal loss of activity during four cycles of the catalytic reaction, indicating that Pd leaching and coke formation were suppressed. Zhu *et al.* reported the hydrogenolysis of GVL to VA over the metal triflates + Pd/C catalyst at 135 °C and 1 atm H₂ for 12 h under a solvent-free condition³⁶; the strong Lewis acid site of metal triflates and oxophilic metal promoted the ring opening of GVL, and further hydrogenation proceeded by the H-radical generated from Pd/C to produce VA.

In contrast with the numerous reports of noble metal-based bifunctional catalysts, only a few studies have examined the use of non-noble metal-based catalysts. Sun *et al.*³⁰ investigated the selective hydrogenation of LA to VA and ethyl valerate over an encapsulated Co metal-based bifunctional catalyst (Co@HZSM-5) using both batch and fixed-bed reactors at 240 °C under 3 MPa H₂ in H₂O or ethanol. In ethanol, 100% LA conversion and a VA + VE mixture yield of 97% were achieved. The Co NPs encapsulated in the framework of the HZSM-5 zeolite showed high stability, as they suppressed Co leaching and sintering under the liquid-phase reaction conditions. Later, the same group investigated coke formation over an acidity-regulated K-modified Ni/HZSM-5 catalyst.³³ After 80 h of continuous LA conversion in a fixed bed reactor, a gradual reduction in the VA + VE mixture yield was noted due to coke formation. Kumar *et al.* reported that the conversion of LA over Brønsted acid-enhanced W-modified Ni/TiO₂³² and W-modified Ni/HZSM-5 at 200 °C and 0.1 MPa H₂ in a fixed bed reactor produced 36% VA yield and 26% VA yield, respectively.³¹

As discussed above, the direct conversion of LA to VA or VE over heterogeneous catalysts without isolating GVL remains a great challenge. The main issues that must be carefully addressed include: (1) the production of mixture of VA and VE, as encountered in previous studies. This lack of product selectivity necessitates additional highly energy-intensive and expensive separation procedures Published on 17 December 2019. Downloaded by University of Saskatchewan on 1/2/2020 7:53:17 PM.

to recover and purify the products. Therefore, the selective production of either VA or VE directly from LA is highly desirable. (2) In most previous studies (Table S1), the conversion of LA was conducted in organic solvents.^{21, 27-30, 35} Because LA is typically produced by the hydrolysis of monosaccharides, polysaccharides, or even directly from lignocellulosic biomass in aqueous medium,⁷ it is logical to perform LA conversion in the same aqueous medium to avoid the highly energy-intensive and expensive recovery of LA from the aqueous reaction medium. In addition, the use of toxic organic solvents in the practical-scale conversion of LA would produce a large amount of organic waste. (3) The extreme scarcity and high cost of noble metals (Pt, 50.86 USD/g; Pd, 31.99 USD/g, Ru, 9.27 USD/g)³⁷ are major drawbacks that prevent practical-scale biofuel production. Thus, the development of a highly efficient and inexpensive non-noble metal-based catalyst is desirable. (4) The highly corrosive nature of LA and the liquid-phase reaction conditions make it difficult to suppress metal leaching during the reaction. Encapsulation of the metal sites in the support framework is a promising solution for suppressing metal leaching,^{29, 30} but the inherently low active material loading and sluggish diffusion of the reactants into the encapsulated active phase lower the catalytic activity. (5) To activate the ring-opening of GVL, acidic sites such as those present on zeolitic supports, metal triflates, AIMCM-41, and SBA–SO₃H are promising,^{27, 30, 33, 38} but the instability of zeolitic supports under hydrothermal conditions and the accelerated coke formation on the acid sites are major drawbacks. Therefore, the acidity of the catalyst must be tuned to optimize the tradeoff between GVL activation and coke formation. (6) Lastly, in most previous cases (Table S1), relatively harsh reaction conditions were used in the conversion of LA (high hydrogen pressure, high temperature, extended reaction time,

and high catalyst-to-feed ratios); such conditions are highly unfavorable for scale-up. Therefore, the development of an economically viable, efficient, and robust non-noble metal-based catalyst for the selective conversion of LA to VA or VE under mild reaction conditions in an environmentally benign solvent is highly desired.

Herein, we demonstrate that a highly-efficient, robust, and non-noble metal-based bimetallic catalyst, Nb-doped Cu on Zr-doped porous silica (Nb-Cu/ZPS), can directly convert LA almost exclusively into VA (>99.8%) under mild reaction conditions (150 °C, 3 MPa H₂, 4 h, catalyst-to-feed ratio of 0.125) in aqueous medium. The VA yield achieved in this study is unprecedentedly high compared to those in previous studies (Table S1). The bimetallic Nb-Cu/ZPS catalyst is also highly active for the conversion of VA to alkyl valerates in high yield under mild reaction conditions (150 °C for 2 h) using various alcohols as the medium. The rationale behind the design of the bimetallic Nb-Cu/ZPS catalyst in this study is as follows: (1) the incorporation of Zr into the porous silica framework can create Lewis acid sites on the surface of the support; these sites can enhance the adsorption strength of carbonyl (>C=O) group-containing substrates through coordination with the unsaturated Zr⁴⁺ ions,³⁹ and (2) the doping of Nb as a promoter on Cu nanoparticles (NPs) not only creates Brønsted acid sites when contact with water molecules,⁴⁰⁻⁴³ but also helps to reduce Cu leaching and aggregation of the Cu NPs during the reaction.

2. Experimental section

2.1 Materials

Pluronic P-123 (molar mass: 5800 g mol⁻¹) and tetraethyl orthosilicate (TEOS, 98% purity) were purchased from Sigma-Aldrich (USA). Zirconium oxychloride (ZrOCl₂, 98% purity), copper(II) nitrate hemipentahydrate (Cu(NO₃)₂·2.5H₂O, 98% purity), and niobium(V) pentachloride (NbCl₅, 99% purity) were procured from Alfa-Aesar (USA). Hydrochloric acid (HCl, 37% aqueous solution), methanol (99.9% purity), ethanol (99.9% purity), isopropanol (99.9% purity), tetrahydrofuran (THF, 99.5% purity), *n*-hexane (99.9% purity), *N*,*N*-dimethylformamide (DMF, 99.9% purity), and acetonitrile (ACN, 99.9% purity) were purchased from Daejung Chemicals (South Korea). LA (98.9% purity), GVL (99.7% purity) and 2,5-hexanedione (2,5-HED, 98.9% purity) were procured from Sigma Aldrich (USA) and used as standards for quantification. The chemicals were used without further purification. Distilled and deionized (DDI) water was prepared using an Aqua Max Basic 363 water purification system equipped with a 0.22 μ m filter (Young Lin Instrument Co., Ltd., South Korea). 5% H₂/Ar (99.999% purity), air (99.9% purity), He (99.999% purity), oxygen (99.999% purity), 10% NH₃/Ar (99.999% purity), and 10% N₂O/He (99.999% purity) were purchased from JC Company (South Korea).

2.2 Catalyst preparation

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2.2.1 Synthesis of Zr-doped porous silica (ZPS)

For the synthesis of ZPS, 0.5 g of Pluronic P-123, 4 mL of DDI water, and 13.3 mL of HCl were mixed and stirred at room temperature until a clear solution was obtained. TEOS (1.15 mL) was then added dropwise to the aqueous solution, and then $ZrOCl_2 \cdot 8H_2O$ (0.162 g) was added into the mixture. The whole mixture was then stirred at 35 °C for one day. The weight ratio of P123:H₂O:HCl:TEOS:ZrOCl₂ in the mixture was 2.9:19.4:69.9:6.7:0.94. The solution was subsequently heated at 90 °C for one day in a beaker on a hot plate. The solid product was recovered by filtration, then washed with DDI water, dried overnight at 100 °C, and calcined at 550 °C for 5 h under air at a flow rate of 30 mL min⁻¹ to produce ZPS. The procedure for synthesis of porous silica (PS) without Zr was the same as that for the production of ZPS, except that $ZrOCl_2$ was not added. To synthesize PS, the weight ratio of P123:H₂O:HCl:TEOS in the mixture was set at 3.33:22.4:66.7:7.67.

2.2.2 Synthesis of bimetallic Nb-doped Cu/ZPS catalysts

ZPS was loaded with Nb and Cu via a wet impregnation method using an aqueous solution of Cu(NO₃).2.5H₂O and NbCl₅. The amount of Nb and Cu loaded on the ZPS support was controlled by adjusting the concentrations of NbCl₅ (in the range 1–6 wt%) and Cu(NO₃)₂·2.5H₂O (in the range 10– 50 wt%). An experimentally desired amount of Cu(NO₃).2.5H₂O was dissolved in 10 mL DDI water prepare Cu(NO₃).2.5H₂O aqueous solution. Because of its high hydrolysis activity, NbCl₅ was first dissolved in 5 mL ethanol and then additional 5 mL DDI water was added to the NbCl₅ ethanol solution. Then the Cu(NO₃).2.5H₂O and NbCl₅ solutions were mixed together, and then the mixture was dropwise added to pre-weighed ZPS. The reaction mixture was stirred at room temperature for 2 h, and the liquid phase was then evaporated at 80 °C. The resulting solid product was calcined at 500 °C for 5 h at a ramp rate of 2 °C min⁻¹ under 5% H₂/Ar gas flowing at 30 mL min⁻¹. The synthesized catalysts are designated as xNb-yCu/ZPS, where x and y represent the experimentally desired weight percentages of Nb and Cu impregnated in the ZPS support, respectively.

2.3 Catalyst characterization

The phase structure and crystallite size were investigated by powder X-ray diffraction (XRD) at a scanning rate of 3–90° (scanning speed: 0.02° s⁻¹) using Cu-K α (λ = 1.5418 Å) Ni-filtered radiation at 40 kV and 50 mA with a D/Max-2500V/PC Rigaku X-ray diffractometer (Japan). The specific surface area, external surface area, and micropore volume of the catalyst were measured using a Belsorp-mini II apparatus (BEL Inc., Japan). The composition of the samples and surface elements were analyzed by X-ray photoelectron spectroscopy (XPS). XPS spectra were recorded using an ESCALAB250 (Thermo Scientific, UK) spectrometer. The binding energy of the C–C bond at 284.8 eV was used as a reference for the peak assignment. The acidity of the catalysts was examined by temperature-programmed desorption of ammonia (NH₃–TPD) using a BELCAT instrument (BEL Inc.). Prior to ammonia adsorption, the catalyst samples were pretreated at 250 °C for 3 h under a flow of He at 30 mL min⁻¹.

The samples were exposed to 10% NH₃ in Ar for 1 h to facilitate the adsorption of NH₃ at 100 $^{\circ}$ C. Desorption of NH₃ from the catalyst samples was carried out from 100 to 1000 °C at a ramp rate of 10 °C min⁻¹ under He flowing at a rate of 30 mL min⁻¹. To investigate the reduction properties of the catalysts, temperature programmed reduction (TPR) was carried out by using a BELCAT instrument. Before the H₂-TPR analysis, each catalyst sample (0.05 g) was subjected to heat treatment under Ar at 250 °C for 1 h. After cooling to 50 °C, the sample was oxidized at 50 °C for 30 min under oxygen (99.9%) atmosphere. The catalysts were reduced by increasing the temperature to 900 °C at a heating rate of 10 °C min⁻¹ under a 5% H₂/Ar flow of 30 mL min⁻¹. The hydrogen consumption was monitored using a thermal conductivity detector (TCD). Pyridine Fourier-transform infrared spectroscopy (Py-FTIR) was used to investigate the nature of the acid sites in the range of 1400-1700 cm⁻¹ at a resolution of 4 cm⁻¹. All samples were pressed into self-standing wafers (15 mg sample + 30 mg KBr), which were then pretreated at 400 °C under a vacuum of 10⁻³ mbar for 1 h prior to pyridine adsorption. After injecting 5 µL of pyridine at 150 °C, the FT-IR cell was saturated for 10 min, followed by evacuation at 150 °C for 30 min to remove excess pyridine. Each sample was scanned 32 times and the Py-FTIR spectra were recorded at room temperature in the transmittance mode. The morphology of the catalysts was determined using field-emission scanning electron microscopy (FE-SEM, Hitachi S-4100, Japan) and high-resolution transmission electron microscopy (HR-TEM, Tecnai G² FEI Co. Ltd., USA). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were collected using a Tecnai G2 instrument operated at 200 kV. The samples were suspended in ethanol and deposited directly on a gold grid prior to analysis. To evaluate corrosion of the catalyst, cyclic voltammetry (CV) was performed in a three-electrode cell configuration using a potentiostat/galvanostat (Model VSP, BioLogic Science Instruments, France). The catalyst-containing electrodes were prepared by suspending ~70 mg of the catalyst and 20 mg of carbon black in 10 mg of polyvinylidene fluoride in N-methyl-2-pyrrolidinone. The slurry was then coated uniformly on a 1 cm²

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stainless steel coupon, which was dried overnight in a vacuum oven at 80 °C. An aqueous solution (85.0 mmol L⁻¹), similar to that used for LA conversion, was used as the electrolyte solution. The reference and counter electrodes were Ag/AgCl and Pt foil, respectively. Prior to the CV measurements, the electrolyte solution was degassed with high-purity N₂. The electrodes were cycled in the voltage window of +0.1 to -0.5 V at a scan rate of 20 mV s⁻¹. A Q50 thermogravimetric analyzer (TGA, TA Instruments, USA) was used to investigate coke deposition on the spent and fresh catalysts under an air flow of 60 mL min⁻¹, at temperatures ranging from 30 to 800 °C, at a heating rate of 10 °C min⁻¹. The loading of Cu and Nb on the ZPS support was measured by using an Optima 7300 V inductively coupled plasma-optical emission spectrometer (ICP–OES).

The surface area of the Cu NPs loaded on the ZPS support was measured via N₂O chemisorption at 75 °C. Typically, a flow of 5% H₂/Ar was used to reduce the catalyst at 350 °C for 30 min, and subsequently, the reactor was cooled from 350 to 75 °C under a He gas flow at 30 mL min⁻¹. Thereafter, 0.5 mL of N₂O was injected via pulse mode through a 988 µL sample loop, and the decomposition of N₂O to N₂ on the surface of the metallic Cu NPs was examined using a gas chromatograph (GC) equipped with a TCD and a column (activated carbon, 250 mm, BELCAT). The surface density of Cu was set to 8.96 g cm⁻³ for measurement of the surface area of the metallic Cu NPs. The N₂O pulse titrations were replicated to avoid possible sub-surface oxidation of the catalyst, which is typically caused by excess pulses. A maximum of three or four injections of N₂O pulses was carried out for each experiment. The surface area of Cu⁰ was calculated using the N₂O titration method based on the equation: N₂O(g) + 2Cu(s) \rightarrow Cu₂O(s) + N₂(g).

CO-diffuse reflectance infrared Fourier transform spectroscopy (CO-DRIFTS) analysis was used to investigate the nature of the metal catalytic sites, the oxidation state of the metals, and coordination mode of the as-synthesized catalysts. A PerkinElmer Frontier spectrometer equipped with a mercury cadmium telluride (MCT) detector and a Harrick Praying Mantis cell (USA) was used for this purpose.

Prior to analysis, the catalyst samples (mixed with KBr) were pretreated at 150 °C under N₂ at a flow rate of 40 mL min⁻¹ for 1 h. The catalyst was then reduced at 450 °C under H₂ flowing at a rate of 40 mL min⁻¹ for 4 h and subsequently flushed with N₂ for 30 min at the same temperature. The samples were then cooled to ambient temperature, and background spectra were collected. The sample was then exposed to a controlled stream of 5 vol% CO in He at a rate of 50 mL min⁻¹ for 1 h. The samples were flushed with N₂ to remove non-adsorbed CO molecules and the IR spectra were collected at ambient temperature. All spectra were converted into Kubelka-Munk units.

To gain insight into the possible interactions between the adsorbate and adsorbent, an adsorption study was conducted at room temperature. The role of Zr in the ZPS support as an active center for interaction with different types of oxygenated functional groups in the reactant was evaluated by using LA, VA, and 2,5-HED as the selected adsorbents. For the adsorption study, 20 mL of a 10000 ppm aqueous solution of each adsorbent was separately transferred to two 25 mL vials, and 100 mg of the PS or ZPS support was added to each vial. The mixtures were sonicated for 10 min and were left undisturbed to allow the catalyst to settle. The catalyst was separated, and the liquid product was analyzed using high-performance liquid chromatography (HPLC).

2.4 Catalyst activity and product analysis

The catalytic reactions for the conversion of LA to VA were performed in a 140 mL stainless steel batch reactor equipped with a mechanical stirrer. Prior to the LA conversion experiments, the assynthesized catalysts were reduced at 500 °C under H₂/Ar atmosphere for 5 h with a temperature ramp of 2 °C min⁻¹. In a typical experiment, 3.4 mmol of LA, 50 mg of the activated catalyst, and 30 mL of DDI water were added to the reactor. The reduced catalyst was immediately charged into the reactor, and the reactor was sealed and purged three times with H₂ and then pressurized to the experimentally desired H₂ pressure at room temperature to suppress air oxidation of Cu NPs. The reactor was heated to various temperatures in the range of 120–200 °C for varying reaction times of 1–4 h with a fixed

stirring rate of 600 rpm. After the reaction, the reactor was rapidly quenched with cold water to cool the reactor to room temperature and then depressurized to atmospheric pressure. 1,6-Hexanediol as an internal standard was added to the reaction mixture. The entire reaction mixture was then collected in a beaker by washing the reactor with DDI water (20 mL \times 2). The used catalyst was separated from the liquid product via filtration with CHMLAB qualitative filter paper (C1.F093.055, Spain). Prior to the HPLC analysis of the liquid product, the product was filtered through a 0.45 µm syringe filter. An HPLC (Waters e2695) equipped with a Bio-Rad Aminex HPX-87H column (300 \times 7.8 mm) and Waters 2487 UV detector (220 nm) was used to quantify the reaction products. The HPLC column temperature was set at 40 °C. The injection volume was 10 µL, and the mobile phase was 0.0013 N H₂SO₄ at a flow rate of 0.5 mL min⁻¹. The conversion of LA and the yield and selectivity of VA were calculated from the HPLC data using Eqs. 1–3:

Conversion (%) =
$$\left(1 - \frac{\text{moles of reacted LA}}{\text{moles of initial LA}}\right) \times 100$$
 (1)

$$Yield (\%) = \frac{moles \, of \, VA}{moles \, of \, initial \, LA} \times 100$$
⁽²⁾

Selectivity (%) =
$$\frac{\text{moles of VA}}{\text{moles of LA converted}} \times 100$$
 (3)

For comparative purposes, the LA conversion in organic solvents was also evaluated. The reaction products collected in organic solvents were analyzed using an Agilent 7890N GC instrument with a time-of flight mass spectrometer (TOF-MS) detector. The GC/TOF-MS was equipped with an auto-injector system (Agilent 7860N) and a Rxi-5Sil-MS column (30 m × 0.25 mm × 0.25 μ m). Typically, 1 μ L of the reaction products recovered after the reaction was injected into the column in split mode (50: 1). The injector temperature was set at 250 °C and the transfer line temperature was fixed at 260 °C. The initial temperature of the column was set at 40 °C with a holding time of 2 min. The temperature was increased to 300 °C at a ramping rate of 10 °C min⁻¹. The detectable mass range for the MS analysis was set at 35–650 *m/z*. An Agilent 6890N instrument equipped with a flame ionization detector (FID) and a Rxi-5Sil-MS capillary column (30 m × 0.25 mm) was used for quantitative analysis of the products collected from the

reactions in organic solvent. A 1.0 μ L aliquot of the product sample was injected at the inlet temperature of 250 °C with the detector temperature set to 250 °C, using a split ratio of 1:10. The initial column temperature was maintained at 40 °C for 2 min, and thereafter ramped to the final temperature of 240 °C at a rate of 10 °C min⁻¹. The conversion of LA and the yield and selectivity of VA were calculated from the GC-FID results using Eqs. 1–3. After the reaction, the number of moles of unreacted reactant and products were quantified from the calibration curves constructed using standard reference compounds by using HPLC analysis for the reactions in aqueous medium and by GC-FID for those in organic solvents (see Fig. S1).

3. Results and discussion

3.1 Catalyst characterization

Fig. 2a shows the XRD patterns of the porous silica (PS), Zr-doped porous silica (ZPS), and the bimetallic Nb-Cu/ZPS catalysts with varying Nb and Cu loadings. The XRD pattern of the PS support exhibited a broad peak centered at 23.2°, which is characteristic of amorphous SiO₂.⁴⁴ The incorporation of Zr into the porous silica did not change the crystallinity of PS, and no peaks associated with ZrO₂ were observed in the profile of ZPS, indicating that the Zr species were well-incorporated into the silica framework or that the particle size of ZrO₂ was below the detection limit of XRD (2 nm).⁴⁵ As shown in Fig. 2b, the appearance of the stretching vibration of the Si–O–Zr bond at 965 cm⁻¹ in the FT-IR spectrum of ZPS, which was not observed in the spectrum of PS, confirmed the incorporation of Zr into the SiO₂ framework.⁴⁶ The XRD patterns of the Nb-Cu/ZPS catalysts showed peaks at 43.3°, 50.2°, and 75.2° attributed to the (111), (200), and (220) planes of Cu⁰ (JCPDS file No. 4-0836), respectively, and the peaks at 22.5°, 28.4°, and 36.4° were attributed to the (001), (100), and (101) planes of Nb₂O₅, respectively (JCPDS file No. 28-317).⁴⁷ The average crystal sizes of the metallic Cu⁰ NPs in the Nb-Cu/ZPS catalysts were evaluated by using the XRD peak corresponding to the (111) plane at 43.6° and the Scherrer equation, and the results are listed in Table 1. When the Nb

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doping level was increased to 6 wt%, the crystallite size of Cu^0 decreased from 35.0 nm (Cu/ZPS) to 24.3 nm (6Nb-40Cu/ZPS), indicating that Nb doping decreased the crystallite size of the Cu NPs. This may be due to suppression of the growth of the Cu NPs in the presence of Nb₂O₅, as discussed in detail in a later section. As shown in Fig. 2a, no shift of the Cu (111) peaks was observed in the XRD profile of the bimetallic Nb-Cu/ZPS catalysts, indicating that alloy formation between the Cu and Nb phases was negligible.

The textural properties of the bimetallic Nb-Cu/ZPS catalysts were evaluated from the corresponding N₂ adsorption–desorption isotherms. As shown in Fig. 2c, the isotherms of the ZPS support exhibited type IV behavior with a H1 hysteresis loop in the p/p_0 range of 0.5–1.0, indicative of a mesoporous structure. The BET surface area of the ZPS support was 658 m² g⁻¹. The external surface area of the ZPS support determined by the t-plot method was 554 m² g⁻¹, which corresponds to 84% of the total BET surface area. This indicates that the ZPS support had a high surface area and large number of exposed active sites, which would facilitate the transport of the bulky LA molecules to the surface of the support. After loading with 40 wt% Cu, the BET surface area decreased slightly to 511 m² g⁻¹. When the Nb doping level of the bimetallic Nb-Cu/ZPS catalysts was increased from 1 to 6 wt%, the BET surface area decreased from 496 to 399 m² g⁻¹. In addition, as shown in Fig. 2d, increasing the Nb doping to 6 wt% resulted in a significant reduction of Nb₂O₅ suppressed the growth of the metallic Cu⁰ NPs; consequently, some of the pores of the ZPS support were blocked by the ultra-small Cu NPs, which nucleated near the surface of the pores.

 N_2O pulse chemisorption analysis was used to further investigate the effect of Nb doping on the size of the Cu NPs in the bimetallic Nb-Cu/ZPS catalysts (Table 2). When the Nb doping level was increased from 0 to 6 wt%, the Cu dispersion increased from 2.8% to 3.5%, the surface area of the Cu NPs increased from 18.1 to 22.4 m² g⁻¹, and the particle size of Cu decreased from 37.1 to 30.0 nm.

This indicates that the use of Nb_2O_5 as a promoter led to an increase in the Cu surface area and Cu dispersion.⁴⁸ These results are consistent with the XRD and N₂ adsorption–desorption results.

The FE-SEM images and elemental mapping data for the catalysts are shown in Fig. S2. The ZPS support comprised spherical particles with an average size of 500–700 nm. EDS mapping of the ZPS support illustrated uniform distribution of Zr throughout the ZPS framework. The overall morphology of 4Nb-40Cu/ZPS was quite similar to that of the ZPS support, indicating that impregnation of the support with the active metals did not change the morphology of the support significantly. The Nb and Cu species were uniformly distributed over the surface of the support. To further investigate the morphology of the catalyst, HR-TEM and HAADF-STEM images of the ZPS support, monometallic 4Nb/ZPS and 40Cu/ZPS, and bimetallic Nb-Cu/ZPS catalysts were collected, as shown in Fig. 3. The unique porous structure of the ZPS support was apparent from the HR-TEM and HAADF-STEM images. No fringes associated with ZrO_2 were observed in the FFT images, indicating that Zr was uniformly distributed throughout the framework of the porous silica (Fig. 3a). The morphology of 4Nb/ZPS was quite similar to that of the support (Fig. 3b), indicating that the low Nb₂O₅ loading did not change the morphology of the ZPS support. The 40Cu/ZPS catalyst comprised spherical Cu NPs (35–40 nm in diameter) uniformly distributed on the surface of ZPS (Fig. 3c). However, large areas of the surface of ZPS were not covered with Cu NPs. In sharp contrast, for 4Nb-40Cu/ZPS, the surface of ZPS was more widely covered by the Cu NPs (Fig. 3d). Compared to that of the Cu NPs in 40Cu/ZPS, the surface of the Cu NPs in 4Nb-40Cu/ZPS was highly crumpled, and the size of the Cu NPs decreased to 30-35 nm in the latter. The interplanar spacings of 0.208 nm and 0.180 nm (Figs. 3d and S3) were attributed to the (111) and (200) planes of Cu⁰, indicating the presence of Cu with a fcc structure (JCPDS file number 04-0836). The interplanar spacing of 0.39 nm (Fig. S3a) indicates the presence of monoclinic Nb₂O₅ (JCPDS file number 04-0836). The HAADF-STEM images of 4Nb/ZPS, 40Cu/ZPS, and 4Nb-40Cu/ZPS (Fig. 3) and their EDS images (Fig. S3b) clearly revealed the uniform

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and homogenous coverage of the surface of ZPS by the Cu and Nb species in the bimetallic 4Nb-40Cu/ZPS catalyst. The drastic change in the morphology of bimetallic 4Nb-40Cu/ZPS compared to that of monometallic Cu/ZPS indicates that Nb doping significantly altered the nucleation and growth of the Cu NPs. The mechanism of formation of bimetallic 4Nb-40Cu/ZPS is schematically represented Fig. 3e. As discussed previously, some dopants (e.g., Zn, Zr, Nb, and Ga) can act as promoters and influence the size and shape of the host nanocrystals by affecting the rate of crystal growth.⁴⁹⁻⁵¹ During crystal growth, the dopant is adsorbed on the facets of the host nanocrystals, thus changing the facet energy, thereby altering the nucleation and subsequent growth rate. Thus, Nb incorporation significantly altered the size and shape of the host Cu NPs.

The chemical composition of the bimetallic Nb-Cu/ZPS catalysts with different Nb doping levels was examined using XPS; the high-resolution Zr 3d, Cu 2p, and Nb 3d spectra are presented in Fig. 4. Prior to the XPS analysis, all the catalysts were reduced by treatment in an atmosphere of 5 vol% H_2/Ar at 500 °C for 5 h. The Zr 3d spectra were fitted to two peaks at 182.8 eV and 185.2 eV, which correspond to Zr $3d_{5/2}$ and Zr $3d_{3/2}$, respectively. These binding energies are higher than those of bulk ZrO_2 at 182.2 eV (Zr 3d_{5/2}) and 184.5 eV (Zr 3d_{3/2}), as referenced to the C–C peak at 284.8 eV,⁵² and are close to those of ZrSiO₄ (183.2 eV and 185.3 eV, respectively).^{53, 54} The shift of the Zr 3d peak to higher binding energy may be due to the formation of Si–O–Zr bonds in ZPS;⁵³ the shift in the binding energies of Zr may be attributed to the higher electronegativity of Si compared to that of Zr. Therefore, the shift in the Zr 3d peak confirmed that the Zr ions were very well incorporated into the silica framework rather than being localized outside the framework as bulk ZrO₂. A doublet Cu 2p_{3/2} peak was observed at 931.9 and 934.0 eV and a doublet Cu $2p_{1/2}$ peak was observed at 952.4 and 954.5 eV (Fig. 4b) in the Cu 2p spectra, with a binding energy difference between the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ doublets of approximately 20.5 eV. The appearance of the Cu²⁺ satellite peak at 942.9 eV in the spectra of the reduced catalysts indicates that Cu⁰ was oxidized when exposed to air during sample collection

and mounting in the XPS sample holder. The area percentage of the Cu^{2+} peak at 934.0 eV decreased significantly from 28.3% to 17.2% when the Nb content was increased from 1 to 6 wt%, indicating that Nb acted as a promoter to suppress the re-oxidation of Cu^{0} . Because the binding energy difference between Cu^{0} and Cu^{+} was very small (0.7 eV), it was difficult to differentiate between the Cu^{+} and Cu^{0} peaks in the Cu $2p_{3/2}$ spectra. The Nb 3d spectra exhibited two peaks at 207.1 eV and 209.8 eV, which were assigned to the Nb⁵⁺ species.⁵⁵ This indicates that most of the Nb in the catalyst was present as Nb₂O₅.

NH₃–TPD was used to characterize the active sites in the as-synthesized catalysts (Fig. 5a, Table 3). The desorption peaks in the temperature ranges of 100–275 °C, 275–500 °C, and 500–600 °C can be attributed to weak, medium, and strong acidic sites, respectively. The NH₃–TPD profile of the ZPS support contained high-temperature desorption peaks in the 700–800 °C region, with a total acidity of 0.88 mmol g⁻¹. The strong acidity of ZPS is due to the presence of Zr in the neutral SiO₂ framework.^{46, 56} After loading Cu onto the surface of ZPS, low-temperature desorption peaks were observed, and the high-temperature desorption peaks shifted towards the low-temperature direction. The wide peaks in the TPD profiles of the bimetallic Nb-Cu/ZPS catalysts in the weak, medium, and strong acidity regions were deconvoluted into five or six peaks. Overall, the total acidity of the bimetallic Nb-Cu/ZPS catalysts increased from 0.83 to 1.08 mmol g⁻¹ when the Nb doping level was increased from 0 to 6 wt%.

Py–FTIR analysis was used to further investigate the types of acid sites in the catalyst (Fig. 5b). The bands at 1450, 1550, and 1488 cm⁻¹ can be assigned to the Lewis acid (L), Brønsted acid (B), and L+B acid sites, respectively. The peaks at 1588 and 1608 cm⁻¹ were assigned to the L sites.^{55, 57} L sites were predominant in the as-synthesized monometallic Cu/ZPS and bimetallic Nb-Cu/ZPS catalysts (coordinated pyridine: 1450 and 1608 cm⁻¹) with fewer B sites (protonated pyridine: 1550 and 1645 cm⁻¹). The presence of Lewis acid sites in the monometallic Cu/ZPS resulted from $Zr^{\delta+}$ in the ZPS

support, and the Nb⁵⁺ sites in the bimetallic Nb-Cu/ZPS catalysts contributed additional Lewis acid sites. When the Nb doping level in the bimetallic Nb-Cu/ZPS catalysts was increased, a low intensity band at 1550 cm⁻¹ began to emerge, indicating the presence of exposed B sites on the surface of the catalyst. The B sites in the bimetallic Nb-Cu/ZPS catalyst resulted from the creation of highly polarized Nb–O bonds in the distorted NbO₆ octahedral and NbO₄ tetrahedral arrangements in Nb₂O₅ after coordination with H₂O molecules.^{40, 43} The total integral area of the bands at 1550 cm⁻¹ and 1450 cm⁻¹ was used to quantify the L and B acid sites; the *L/B* ratios of the catalysts are presented in Table 3. When the Nb doping level was increased from 1 to 6 wt%, the *L/B* ratio increased significantly from 3.91 to 5.78. The enrichment of L sites with increasing Nb content is attributed to the presence of unsaturated Nb⁵⁺ cations in the exposed Nb₂O₅.^{40, 43, 58}

The reducibility of the active sites in the catalysts was evaluated by H_2 -TPR analyses (Fig. 5c). A small and broad peak centered at 690 °C was observed in the profile of the ZPS support; the low H_2 uptake (0.06 mmol g_{cat}^{-1}) of the support indicates the absence of reducible metal on the surface of ZPS as Zr^{4+} is an irreducible cation below 800 °C.⁵⁹ On the other hand, low-temperature H_2 uptake peaks were observed in the profiles of the monometallic Cu/ZPS and bimetallic Nb-Cu/ZPS catalysts, indicating the reduction of easily reducible CuO species. As listed in Table 3, the H_2 uptake increased from 0.568 to 0.601 mmol g_{cat}^{-1} when the Nb doping level of the bimetallic Nb-Cu/ZPS catalysts was increased from 1 to 6 wt%. The reduction of highly-dispersed CuO to Cu⁰ is known to occur via a two-step reduction process: Cu²⁺ is reduced to Cu¹⁺ at temperatures below 250 °C and Cu¹⁺ is reduced to Cu⁰ at temperatures above 250 °C.⁶⁰ The strong interaction of Cu²⁺/Cu¹⁺ species with the ZPS support may account for the high-temperature reduction peaks centered around 270–510 °C.⁶⁰ The H₂–TPR profile of 40Cu/ZPS showed four distinguishable reduction regions at temperatures of 270–510 °C, and 330 °C are attributed to the reduction of isolated Cu²⁺ species and the reduction of highly-dispersed

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CuO crystallites located on the external surface and in the pores of the ZPS support, respectively. The high-temperature peaks at 429 °C and 510 °C are assigned to the reduction of Cu²⁺–O–Zr or Cu⁺–O–Zr structures and the reduction of CuO in the bulk phase, respectively.¹⁸ Nb doping significantly changed the reduction behavior of CuO. In the Nb doping range of 1–4 wt%, the number of reduction peaks was reduced from four to three, with lowering of the reduction temperature. In contrast with monometallic Cu/ZPS (510 °C), no high-temperature reduction peak was observed in the profile of bimetallic Nb-Cu/ZPS, suggesting that the reduction temperature of bulk CuO decreased. This difference indicates that the Nb dopant acted as a promoter to decrease the reduction temperature by suppressing the growth of the Cu NPs, which is consistent with the XRD and the Cu dispersion results.

To further understand the reductive behavior of bimetallic Nb-Cu/ZPS, CO-DRIFT was employed to investigate possible changes in the electronic states of Cu due to Nb doping. CO-DRIFT has previously been used to explore the effects of the electronic structure on the performance of catalysts comprising a metal (Mo, Ru, Pt, Rh) on acidic (zeolites, Nb₂O₅, TiO₂) and neutral (SiO₂) supports.⁶¹⁻⁶³ Fig. 5d shows the DRIFT spectra of CO adsorbed on 40Cu/ZPS, 4Nb-40Cu/ZPS, and Nb₂O₅. The CO-DRIFT profile of monometallic 40Cu/ZPS showed two broad peaks of adsorbed CO at 2050–2220 cm⁻ ¹, which were further deconvoluted into six assignable peaks. The region below 2130 cm⁻¹ (2127 and 2110 cm⁻¹ for the 40Cu/ZPS sample) is attributed to CO weakly adsorbed on metallic Cu⁺ in a linear geometry through π -bond interaction.^{64, 65, 66, 67} The band at 2083 cm⁻¹ is attributed to CO adsorbed on highly dispersed nano-structured metallic Cu in the form of Cu⁰-CO.⁶⁸ On the other hand, the adsorption peaks appearing at 2174 and 2153 cm⁻¹ are attributed to the symmetric and asymmetric stretching vibrations of Cu^+ –(CO)₂ species, respectively.⁶⁹ The peak at 2200 cm⁻¹ is assigned to the characteristic peak of Cu²⁺-CO species.⁶⁵ After doping the 40Cu/ZPS catalyst with 4 wt% Nb, all the deconvoluted peaks of CO adsorbed on Cu, except for the peak at 2200 cm⁻¹, shifted to higher wavenumber. This blue shift is caused by the Lewis-acidic Nb₂O₅, which lowers the electron density of

the Cu NPs in 4Nb-40Cu/ZPS. In the case of Nb₂O₅, no CO adsorption peak was observed, which confirms that the blue shift is caused by the Lewis acid characteristics of Nb₂O₅. The CO-DRIFT results clearly indicate that the major species in the Cu NPs in the bimetallic 4Nb-40Cu/ZPS are Cu/Cu^+ rather than Cu^{2+} , which agrees well with the XPS data. The presence of highly populated Cu^+ species on the 4Nb-40Cu/ZPS catalyst can be explained by approximately 0.5 V above the valance band edge of Nb_2O_5 .^{70, 71} Notably, the presence of Cu^0/Cu^+ species can facilitate hydrogenation/hydrodeoxygenation.^{72, 73} The decrease in electron density of Cu⁺ species in the 4Nb-40Cu/ZPS catalyst can increase their reduction temperatures and keep the reducing metal in their high oxidation state.^{74, 75} For example, the electron withdrawing characteristic of Mn₂O₄ created low electron density over Cu NPs, resulting in increasing the Cu⁺ fractions rather than Cu⁰ in Cu@Mn₂O₄.⁷⁵ Similarly, the Lewis acid characteristics of Nb_2O_5 decreased the electron density of Cu^+ species, which would increase the reduction temperature. On the other hand, the H_2 -TPR profiles revealed that the bimetallic Nb-Cu/ZPS catalysts exhibited slightly lower reduction temperatures (Fig. 5c). This discrepancy could be because of the decrease in Cu NPs size by the Nb₂O₅ doping, which facilitate the reduction reaction.

3.2 Catalyst evaluation

The conversion of LA over the ZPS support, monometallic Cu/ZPS catalysts, and bimetallic Nb-Cu/ZPS catalysts was examined at 150 °C using an initial H₂ pressure of 3 MPa, a catalyst-to-feed ratio of 0.125, and a reaction time of 2 h in aqueous medium; the results are listed in Table 4. The LA conversion and GVL yield achieved with the ZPS support were 25.9% and 19.8%, respectively, accompanied by the production of a small amount of α -angelica lactone (α -AL, see Fig. S4 for the HPLC results). These observations suggest that the Lewis acid sites in the ZPS support were somewhat active for the direct cyclization of LA. It was previously reported that Zr-based catalysts such as ZrO₂ and UiO-66 are active in the conversion of LA to GVL in the presence of both external and internal

hydrogen sources;^{18, 19} this is possible because Zr-containing catalysts with acidic Zr⁴⁺ sites can activate the carbonyl group of LA.^{19, 39} The detailed reaction mechanism is discussed in Section 3.6. After verifying the presence of active acid sites in the ZPS support for the conversion of LA, the effect of impregnation of ZPS with Cu metal on the hydrogenation reaction was evaluated. After Cu loading, both the LA conversion and GVL yield increased; when the Cu loading in the monometallic Cu/ZPS catalysts was increased from 10 to 40 wt%, the LA conversion increased from 50.2% to 80.3% and the GVL yield increased from 45.0% to 75.8% (entries 3–6, Table 4). Further increasing the Cu loading to 50 wt% resulted in a slight decrease in the LA conversion and GVL yield, plausibly due to the decreased availability of the Zr-based Lewis acid sites required for the adsorption and conversion of LA due to the extensive coverage of Cu on the ZPS surface. As indicated in Table 1, the BET surface area decreased significantly from 511 to 429 m² g⁻¹ when the Cu loading was increased from 40 to 50 wt%. Even though GVL was produced in high yield over the monometallic Cu/ZPS, the targeted product VA was not observed in the reaction mixture. The liquid mixture had a light brick red coloration due to leaching of Cu metal from the monometallic Cu/ZPS catalysts (Fig. S5a).

When the Nb doping level in the bimetallic Nb-Cu/ZPS catalysts was increased from 1 to 4 wt%, the LA conversion increased from 81.5% to 95.6% and the VA yield increased significantly from 21.0% to 92.5%, while the GVL yield decreased significantly from 58.0% to 2.2% (entries 8–11). As indicated in Table S1, the VA yield over 4Nb-40Cu/ZPS was unprecedentedly high compared to those of previously reported noble metal and non-noble metal-based catalysts, even under much milder reaction conditions. In addition, the aqueous mixture collected after the reaction was completely transparent and colorless (Fig. S5b), which demonstrates that Nb doping effectively suppressed oxidation of the Cu⁰ NPs during the reaction. Leaching of the Cu-based catalyst is explained in detail in Section 3.4. Further increasing the Nb doping level to 6 wt% (6Nb-40Cu/ZPS) did not change the LA conversion or VA yield significantly because the increase in the Nb content from 4 to 6 wt% did not

significantly affect the Cu dispersion (Table 2) or acidity (Table 3) of the bimetallic catalysts. To investigate the effect of Nb on LA conversion, the reaction was conducted over the Cu-free catalyst, i.e., 4Nb/ZPS (entry 13). Under the optimized reaction conditions (150 °C, 3.0 MPa), 26.7% LA conversion with GVL as the major product was achieved with 80.9% selectivity, indicating that Nb₂O₅ effectively facilitated the conversion of LA to GVL.

Having confirmed that Nb doping of Cu/ZPS could trigger the conversion of GVL to VA, the activation energy for LA conversion and VA production were calculated using the time-course reaction data and the Arrhenius equation, as shown in Figs. 6a and b, respectively. The activation energy for LA conversion decreased significantly from 55.2 to 27.7 kJ mol⁻¹ when 4 wt% Nb dopant was added to the 40Cu/ZPS catalyst. When the Nb doping level in the 40Cu/ZPS catalysts was increased from 2 to 4 wt%, the activation energy for the production of VA decreased from 69.2 to 51.0 kJ mol⁻¹. This indicates that the bimetallic Nb-Cu/ZPS catalyst enhanced both the LA conversion and VA selectivity. The turnover frequency (TOF, h⁻¹) of the bimetallic Nb-Cu/ZPS catalysts with varying Nb doping levels was calculated using Eq. 4, and the results are shown in Fig. 6c.

$$TOF(h^{-1}) = \frac{VA \text{ produced (mole)}}{Cu \text{ loading (moles)} \times Cu \text{ dispersion } \times \text{ reaction time (h)}}$$
(4)

Increasing the Nb doping level from 1 to 4 wt% induced an approximately four-fold increase in the TOF from 0.011 to 0.038 h⁻¹. Further increasing the Nb doping level to 6 wt% resulted in a slight decrease in the TOF to 0.037 h⁻¹. Based on the amount of total Cu metal in the bimetallic 4Nb-40Cu/ZPS catalyst, TOF was 81.5 mmol VA $g^{-1}C_{u}$ h⁻¹, a value which is much larger than TOF of noble metal-based Pt/HMFI catalyst (33 mmol VA $g^{-1}P_{t}$ h⁻¹)⁷⁶. The LA conversion, VA selectivity, activation energy, and TOF data clearly demonstrate the significant role of Nb doping in the one-pot conversion of LA to VA.

To further investigate the roles of Zr and Nb in the bimetallic Nb-Cu/ZPS catalyst, the adsorption of various types of molecules on the surface of PS, ZPS, and 4Nb-40Cu/ZPS was investigated. The

adsorbents evaluated herein include LA, which has one carboxylic end group and one ketone group, VA, which has one carboxylic end group, and 2,5-hexanedione (2,5-HED), which has two ketone groups. VA and 2,5-HED were selected for evaluating the adsorption behavior of unifunctional catalysts. As shown in Fig. 7a, the amount of molecules adsorbed increased significantly when Zr was incorporated into the silica framework. This indicates that the Lewis acid sites associated with $Zr^{\delta+}$ enhanced the adsorption of oxygen-containing molecules. For the ZPS support, the adsorption followed the order: VA \approx LA >> 2,5-HED, indicating that the ketone group interacted less strongly with the $Zr^{\delta+}$ -based-Lewis acid sites compared to the carboxylic acid group. The amounts of LA, VA, and 2,5-HED adsorbed on the surface of the 4Nb-40Cu/ZPS catalyst decreased slightly compared to those on the ZPS support because some of the $Zr^{\delta+}$ sites were covered with Cu NPs. Fig. 7b presents a plausible mechanism for the adsorption and conversion of LA to generate 4-hydroxypentanoic acid (4-HPA). The carboxylic acid group of LA is adsorbed on a Lewis acid site of $Zr^{\delta+}$, and the LA ketone group is hydrogenated to an alcohol group over the Cu site to produce 4-HPA. Based on the discussion thus far, the adsorption order of the oxygen-containing molecules can be arranged according to the polarity of the group; carboxyl group > hydroxyl group > ester group > ketone carbonyl group. To verify this, the adsorption study was extended to GVL and D- α hydroxy isovaleric acid (HVA). We selected HVA (which has both the carboxyl group and hydroxyl group as in the case of 4-HPA) because 4-HPA is not available- As shown in Fig. S6, the amount of HVA adsorbed was much higher than GVL. This indicates that 4-HPA does not desorb well from the catalyst surface, and thus is further dehydrated to form GVL. In order to confirm the proposed reaction mechanism, LA conversion was conducted at a low temperature of 100 °C under 1 MPa H₂ in aqueous medium over the 40Cu/ZPS catalyst, and the reaction mixture was analyzed using GC-TOF/MS. As shown in Fig. S7, 4-HPA was detected in the reaction mixture, which clearly indicates that 4-HPA was a reaction intermediate formed by hydrogenation of the ketone group of LA.

3.3 Optimization of the reaction conditions in aqueous medium

In the previous section, we discussed the effectiveness of 4 wt% Nb doping of Cu/ZPS for the onepot direct cascade conversion of LA to VA under mild reaction conditions in aqueous medium. Here, the reaction conditions were varied to optimize the LA conversion and VA selectivity using the 4Nb-40Cu/ZPS catalyst. Fig. 8a shows the effect of temperature on the LA conversion and product yields at a catalyst-to-feed ratio of 0.125 and an initial H₂ pressure of 3 MPa for 2 h of reaction. At the low reaction temperature of 120 °C, 70.5% LA conversion, 45.7% VA yield, and 20.5% GVL yield were obtained, indicating that this low temperature could activate LA conversion or the ring-opening of GVL in the presence of the catalytic system. Further, as shown in Fig. S8, 3-pentenoic acid (3-PEA) was detected in the reaction mixture, indicating that 3-PEA is a reaction intermediate formed by the ring-opening of GVL. When the temperature was increased to 150 °C, the LA conversion increased to 95.6% and the VA yield increased to 92.5%, while the GVL yield was very low (2.2%). This indicates that a relatively mild reaction temperature of 150 °C was sufficient to activate the conversion of LA and ring-opening of GVL over the 4Nb-40Cu/ZPS catalyst. When the temperature was further increased to 200 °C, complete conversion of LA and GVL was observed. On the other hand, the VA yield leveled off at approximately 93% at temperatures of 150–200 °C because of the formation of other products. These may include side products such as 1,4-pentanediol (1,4-PDO, which could be produced by the breakage of the C–O bond of O=C–O in GVL and subsequent hydrogenation), methyl tetrahydrofuran (MTHF, which can be produced by the dehydration of 1,4-PDO), pentanol (which can be produced by the hydrogenation of VA), and/or 5-nonanone (which can be produced by ketonization between PA molecules). As shown in Fig. S9a, 1,4-PDO, MTHF, and 5-nonanone were observed in the reaction mixture when THF was used.

The time-course of the reaction was monitored under conditions employing a temperature of 150 °C, initial H₂ pressure of 3 MPa, and catalyst-to-feed ratio of 0.125 (Fig. 8b). As the reaction time

approached 1 h, the yield of the intermediate GVL increased to 29.4%, while the VA yield was low (18.7%). Further increasing the reaction time to 2 h resulted in a significant decrease in the GVL yield to 2.2% and an increase in the VA yield to 92.5%. Further increasing the reaction time to 4 h did not decrease the VA yield, indicating that VA was stable in the reaction mixture under these mild conditions.

The effect of pressure on the conversion of LA at 150 °C with a catalyst-to-feed ratio of 0.125 in the reaction for 2 h is shown in Fig. 8c. Low H₂ pressures of 1–2 MPa were not sufficient for the one-pot conversion of LA to VA. At 1 MPa H₂, the major product was GVL, while at 3 MPa H₂, the LA conversion increased to 95.6% and the VA yield increased to 92.5%. Further increasing the H₂ pressure to 4 MPa resulted in a slight decrease in the VA yield to 89.7% due to the formation of side products such as 1,4-PDO.

When the catalyst-to-feed ratio was decreased from 0.125 to 0.0625 at 150 °C using 3 MPa H₂ for 2 h, the LA conversion decreased from 94.6% to 73.0%, and the VA yield decreased from 92.8% to 60.3% (Fig. 8d). On the other hand, when the catalyst-to-feed ratio was increased two-fold from 0.125 to 0.250, almost complete conversion of LA to VA (99.1% yield) was achieved. Thus, it can be concluded that at the higher catalyst loading, complete conversion of LA to VA could be achieved, while the generation of other products was suppressed. When the LA concentration was increased from 1.0 to 1.6 wt% at 150 °C using 3 MPa H₂ for 2 h, the LA conversion increased from 88.9% to 96.1%, and the VA yield increased from 62.2% to 90.1% (Fig. 8e)

3.4 Solvent screening and Cu metal leaching

As discussed in the Introduction, the use of water as the reaction medium in the conversion of LA is expedient because of its environmental friendliness. To investigate the other beneficial effects of water as a reaction medium, LA conversion was conducted in different solvents over 40Cu/ZPS and 4Nb-40Cu/ZPS at 150 °C under 3 MPa H₂ using a catalyst-to-feed ratio of 0.125, over the course of 2 h

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(Fig. 9). The LA conversion in the various solvents followed the order: *N*,*N*-dimethylformamide (DMF) \approx water (>95%) > methanol (80.5%) > tetrahydrofuran (THF, 75.5%) > *n*-hexane (60.1%). Although high LA conversion was achieved in DMF, the product mixtures contained a large amount of residual GVL (58.3%), and thus the targeted VA yield was much lower (15.8%) than that achieved in water (92.5%). When *n*-hexane was used, the low solubility of LA in the hydrophobic solvent resulted in low LA conversion. The selectivity for VA achieved with bimetallic Nb-Cu/ZPS was much higher in aqueous medium than in organic solvent because the enhanced Brønsted acidity of Nb₂O₅ in aqueous medium facilitated the conversion of the intermediate GVL by activating the ring-opening reaction.^{40, 43} In THF, the side products 1,4-PDO, 5-nonanone, and MTHF were also detected (Fig. S9); methyl valerate was observed in methanol; dihydro-3,5-methyl-2(3H)-furanone was observed in DMF; and 4hydroxy-2-pentenoic acid was observed in hexane.

In light of the previous observation of leaching of Cu metal from the Cu/ZPS catalyst in aqueous medium, Cu leaching in the various solvents with different polarities (including isopropanol (IPA), methanol, ethanol, THF, acetonitrile (ACN), and DMF) was evaluated (Fig. 9b). After the reaction, the IPA, methanol, ethanol, and THF solutions were blue due to dissolution of the metallic Cu NPs from the catalyst to generate solvated Cu²⁺ ions. The dissolved Cu²⁺ ions could be stabilized by forming chelates with the carboxylic acid groups of LA in the reaction media. In ACN and DMF, the reaction mixture was brownish because N-containing solvents such ACN and DMF can act as reducing agents or protecting agents to stabilize the Cu NPs.^{77, 78} The color change in the organic solvents indicates that the Cu NPs of the monometallic Cu/ZPS were highly susceptible to leaching during the conversion of LA. On the other hand, as shown in Fig. 9a, the reaction over 4Nb-40Cu/ZPS generated transparent and colorless solutions in all the solvents tested in this study. This indicates that Cu leaching from the bimetallic Nb-Cu/ZPS catalyst was effectively suppressed, which was further confirmed by ICP–OES (Fig. S10). To further evaluate the Cu leaching, the redox properties of the monometallic Cu/ZPS and

bimetallic Nb-Cu/ZPS catalysts were evaluated via CV measurements in aqueous LA solution. The CV profiles of the Cu NPs, 40Cu/ZPS, 8.0 wt% Nb loaded on Cu NPs (8Nb92Cu), and 4Nb-40Cu/ZPS are shown in Fig. 9c. The CV profile of the Cu NPs exhibited two broad redox peak pairs centered at – 0.14/-0.24 V during the cathodic and anodic sweeps, which are attributed to the reduction of Cu²⁺ to Cu⁰ and oxidation of Cu⁰ to Cu²⁺, respectively. 40Cu/ZPS exhibited a similar broad redox peak pair centered at -0.21/-0.31 V; the shift of these peaks to more negative potential is attributed to the change in the electronic conductivity of the Cu NPs when loaded on ZPS. On the other hand, no redox peak pair was observed for 8Nb92Cu and 4Nb-40Cu/ZPS, indicating that the redox reaction caused by Cu leaching was effectively suppressed. This suggests that the Cu⁺ species in the Cu NPs in the 4Nb-40Cu/ZPS catalysts are highly stable in the presence of Nb₂O₅, and thus the oxidation of Cu⁺ to Cu²⁺ is effectively suppressed.⁷⁰ As discussed previously, active metal leaching is one of the most deleterious issues in the conversion of LA in various media.^{18, 21, 25, 27-29, 79-81} Leaching of the base metal can be effectively suppressed by re-oxidation of the metal during the reaction, which can be achieved either by facilitating H₂ transfer to the catalyst surface or by doping the host material with metals or metal oxides to tune the electronic states, which can promote dispersion and reduction of the metals and enhance the interaction between the active sites and the support.^{17, 50} For example, Zhang et al.¹⁷ reported the conversion of LA into GVL over a bimetallic Cu-Ag (1:1 ratio) catalyst; doping with an equimolar amount of Ag suppressed Cu leaching by maintaining Cu in the metallic state during the reaction in THF.

3.6 Reaction pathway

Based on the discussion thus far, a plausible reaction pathway for the direct conversion of LA to VA over the bimetallic Nb-Cu/ZPS catalyst was proposed (Scheme 2). As discussed in the previous sections, the reaction intermediates formed in the reactions involving incomplete conversion of LA include 4-HPA, α -AL, GVL, and 3-PEA. The direct conversion of LA to VA involves several steps

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that depend on various factors such as the concentration and species of the acidic sites, the metallic sites available for hydrogenation, the solvent polarity, and the reaction parameters (temperature, pressure, and catalyst-to-feed ratio). In the case of the bimetallic Nb-Cu/ZPS catalyst, the carbonyl group of LA is first adsorbed on the Lewis acid sites in the ZPS support $(Zr^{\delta+})$. LA then undergoes hydrogenation over the Cu NPs to form 4-HPA. In our recent previous study⁸² and a study by others,⁸³ Cu-based catalysts were found to be active towards the selective hydrogenation/hydrodeoxygenation of aryl ketones. After the hydrogenation step, 4-HPA undergoes intramolecular cyclization to form GVL via dehydration over the acid sites.⁸⁴ During the cyclization of 4-HPA, one water molecule is removed to form GVL, which is a very strong and hydrothermally stable intermediate. An alternative pathway for producing GVL is intramolecular cyclization of LA and subsequent removal of water to produce α -AL. To verify α -AL as an intermediate for producing GVL and VA, α -AL was converted over the bimetallic Nb-Cu/ZPS, and the results are shown in Fig. S11 and Table 4; high-yield VA was achieved and residual GVL was observed, while other chemical species were not detected. The Brønsted acid sites of Nb₂O₅ that are generated in aqueous media can donate an activated hydrogen to GVL, converting GVL into a stable carbenium ion and producing 3-PEA by proton elimination.⁸⁵ The role of Nb₂O₅ as the Brønsted acid site was confirmed by the reaction over the monometallic Cu/ZPS catalyst without Nb₂O₅, in which GVL was the major product (Table 4). In contrast, the bimetallic Nb-Cu/ZPS catalyst yielded VA as the main product and GVL as a minor product. Brønsted acid sites are reportedly created in Nb₂O₅ upon contact with water;^{40, 43} these sites can accelerate the conversion of GVL to 3-PEA. It is noted that Lewis acid (e.g., metal triflates) is also effective in the ring opening of GVL to produce 3-PEA.³⁶ 3-PEA is then converted into the final targeted product, VA, by hydrogenation of the C=C bond over the Cu NPs. As reported previously, the conversion of GVL is the rate-limiting step in the direct conversion of LA to VA because of the high stability of GVL. As shown in Table 4, the conversion of GVL to VA was promoted when the Nb₂O₅ doping level was increased to

6 wt%, indicating that this small amount of Nb₂O₅ can provide sufficient Brønsted acid sites for the effective conversion of highly stable GVL to VA. It is noted that the bimetallic Nb-Cu/ZPS catalyst is also effective in the direct conversion of LA to VEs and the conversion of VA to VEs when short-chain alcohols were used as the reaction medium (Fig. S12). For example, when methanol was used, the valerate methyl ester yield was 67.4% directly from LA and 98.0% from VA. This suggests that the cascade conversion of LA into methyl valerate was effectively proceeded over the bimetallic Nb-Cu/ZPS.

3.7 Catalyst recyclability

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To investigate the reusability and stability of the bimetallic 4Nb-40Cu/ZPS catalyst, five consecutive cycles of LA conversion were carried out at 150 °C under 3 MPa H₂ using a catalyst-tofeed ratio of 0.125 and a reaction time of 2 h in aqueous medium (Fig. 10a). After each reaction, the spent catalyst was recovered from the reaction mixture by filtration and washed twice with DDI water to remove any organic species deposited on the catalyst. The spent catalyst was then dried at 80 °C overnight in a vacuum drying oven and reused for the next run without an additional activation step. After five consecutive cycles, the LA conversion decreased slightly from 95.6% to 90.3%, and the VA yield decreased slightly from 92.5% to 86.0%. The slight decrease in the catalyst activity may be due to various factors, such as oxidation of the active metal phase, deposition of coke on the surface of the active sites of the catalyst, or leaching of the active metal. To determine the major cause of catalyst deactivation, the spent catalyst recovered after five cycles was analyzed (Figs. 11b-g). The XRD pattern of the spent catalyst clearly revealed that some of the metallic Cu was oxidized to the Cu₂O phase. The appearance of peaks at 42.4° and 61.5° confirmed the formation of the Cu oxide phase in the form of Cu₂O. As listed in Table 1, the crystallite size of the Cu NPs determined from the data for the (111) plane of Cu⁰ increased slightly from 24.8 nm (fresh catalyst) to 30.4 nm (spent catalyst). As shown in Figs. 11d-e, some aggregation of the Cu NPs was observed in the spent catalyst. The increase

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in the crystallite size and particle size of the Cu NPs in the spent catalyst caused a slight decrease in the Cu dispersion from 3.4% to 3.2% (Table 2). Elemental mapping of the spent catalyst clearly showed the uniform distribution of metallic Cu and Nb over the ZPS support (Fig. 10f). To investigate possible coke formation, TGA data were acquired for the fresh and spent catalysts (Fig. 10c). Prior to TGA, the catalyst sample was subjected to heat treatment under N₂ environment at 100 °C for 1 h to remove physically adsorbed water and other gaseous impurities. The slight weight loss below 120 °C is due to the evaporation of water or other volatile species that were adsorbed on the catalyst surface. The weight of the fresh catalyst increased to 103% at low temperatures in the range of 140-300 °C, while the weight of the spent catalyst did not change much in this temperature range. Taking into account the decomposition of light, carbonaceous deposits on the catalyst below 300 °C,⁸⁶ the stability of the weight of the spent catalyst below 300 °C is attributed to competition between the weight loss caused by coke combustion and weight increase caused by the oxidation of Cu⁰. Because some fraction of the metallic Cu^0 NPs was oxidized to Cu_2O during the reaction (as shown in Fig. 10b), the difference in the weight increase of the fresh and spent catalysts (4 wt%) is the result of competition between further Cu oxidation to CuO (weight increase) and combustion of coke (weight loss). Quantification of the amount of coke deposited on the surface of the catalyst is difficult as the Cu₂O content is unknown. However, assuming that no Cu was oxidized during the reaction, the amount of coke was about 4 wt%. The amount of coke formed in the spent catalyst was small, which is an advantage of the low reaction temperature, and resulted in only a slight decrease in the total acidity (see Table 3). As discussed in the previous section, metal leaching is a major issue in liquid-phase LA conversion. A negligible amount of Cu was leached from the bimetallic Nb-Cu catalysts after five consecutive runs. The loss of Cu from the spent 4Nb-40Cu/ZPS catalyst after five runs (Fig. 10g) was very small (0.9%), while that of spent 40Cu/ZPS recovered after one run was much higher (8.5%). This indicates that Cu leaching was suppressed in the bimetallic Nb-Cu/ZPS catalyst. Notably, only a few studies have reported reduced Cu

leaching under acidic conditions via heteroatom doping (e.g., Nb, Zr, and Ag). Hammes et al.⁵⁰ observed that doping with 1 mol% Nb effectively reduced Cu leaching during the conversion of HCl to chlorine at high temperature (300-370 °C). Very recently, Zhou et al.¹⁷ reported that doping Ag over Cu/Al₂O₃ significantly reduced Cu leaching via the strong geometric and electronic effects between Cu Published on 17 December 2019. Downloaded by University of Saskatchewan on 1/2/2020 7:53:17 PM. and Ag. The spent catalyst recovered after five consecutive runs was heat-treated at 500 °C under 5% H₂/Ar for 3 h to reduce the Cu₂O phase to metallic Cu⁰. The re-activated catalyst was then utilized for LA conversion. As shown in Fig. S13, the color of the catalyst changed from black (fresh catalyst) to brown (after the fifth run), and again to black after re-activation. In the sixth run with the re-activated catalyst (Fig. 10a), the LA conversion and VA selectivity were almost identical to those of the fresh catalyst, even without a coke-burning step. This clearly indicates that coke formation on the surface of the spent catalyst had a negligible effect on the catalyst performance. To further enhance the catalyst stability under low conversion conditions, a reusability test was performed at the low reaction temperature of 120 °C (Fig. S14). The activity of the 4Nb-40Cu/ZPS catalyst was maintained up to the 4th run, even at a low conversion rate, which confirms its excellent stability during the conversion of LA to VA.

4. Conclusion

In summary, levulinic acid (LA) was converted to valeric acid (VA) via one-pot, direct, cascade conversion over a catalyst consisting of bimetallic non-noble metal-based Nb-doped Cu on a Zr-doped porous silica (Nb-Cu/ZPS) support in aqueous medium. Complete conversion of LA to VA in high yield (99.8%) was achieved under mild reaction conditions (temperature of 150 °C, H₂ pressure of 3 MPa, and reaction time of 4 h), along with a high turnover frequency of ~300 h⁻¹. The bimetallic Nb-Cu/ZPS catalyst was also effective for the conversion of VA to valeric esters in various C1–C5 alcohols. Nb doping increased the surface coverage of the Cu nanoparticles (NPs) on the ZPS support, decreased the size of the Cu NPs, and increased the dispersion of Cu. The presence of Zr in the SiO₂

framework enhanced the adsorption of LA via the carboxylic acid group of the former. The ketone group of LA was then hydrogenated to produce 4-hydroxypentanoic acid, and subsequent cascade dehydration, ring-opening, and hydrogenation reactions generated VA directly from LA. The Lewis and Brønsted acidities associated with Nb₂O₅ and the ZPS support, along with the metallic Cu⁰ sites, promoted the catalysis of the one-pot direct conversion reaction. Leaching of Cu during the conversion of LA and coke formation on the surface of the bimetallic Nb-Cu/ZPS were both highly suppressed; thus, the activity of the catalyst could be restored by re-activation under reducing conditions. The highly efficient and non-noble metal-based Nb-Cu/ZPS catalyst developed for the direct conversion of LA to VA in aqueous medium is highly promising for the cost-effective and sustainable production of biofuel from lignocellulosic biomass.

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Table 1. Metal loading, Cu crystallite size, and textural properties of ZPS support and bimetallic Nb-Cu/ZPS catalysts

Catalyst	Nb/Cu loading (wt%)	Cu crystallite size (d ₁₁₁) (nm)	S. A. ^a (m ² g ⁻¹)	$\frac{S_{ext}{}^{b}}{(m^2 g^{-1})}$	$V_{micro}^{c}^{c}$ (cm ³ g ⁻¹)	V_{meso}^{d} (cm ³ g ⁻¹)	V_{total}^{e} (cm ³ g ⁻¹)	Mean pore diameter (nm)

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ZPS	N.A. ^f	-	658	554	0.146	0.336	0.482	4.059
40Cu/ZPS	0/40.6	35.0	511	413	0.045	0.296	0.341	4.347
50Cu/ZPS	N.A. ^f	42.5	429	324	0.024	0.229	0.253	3.988
1Nb-40Cu/ZPS	0.99/39.0	26.4	496	407	0.042	0.290	0.332	4.362
2Nb-40Cu/ZPS	2.01/39.9	26.1	466	386	0.032	0.287	0.318	4.351
3Nb-40Cu/ZPS	2.98/39.2	25.5	434	364	0.014	0.281	0.295	4.312
4Nb-40Cu/ZPS	3.96/38.6	24.8	415	343	0.025	0.297	0.322	4.188
6Nb-40Cu/ZPS	5.89/37.4	24.3	399	330	0.036	0.236	0.272	4.144
4Nb-40Cu/ZPS-S ^g	3.82/38.1	30.4	394	318	0.023	0.289	0.312	4.157

^aSurface area as measured by the BET method

^bExternal surface area as determined by the t-plot method

^cMicropore volume

^dMesopore volume

^eVolume adsorbed at $P/P_o = 0.99$

^fN.A.: not available

^gSpent catalyst after five consecutive runs

Table 2. Dispersion and particle size of Cu NPs in monometallic Cu/ZPS and bimetallic Nb-
Cu/ZPS catalysts, as determined by N ₂ O chemisorption

Catalyst	$D_{C\mu}^{a}(\%)$	$SA_{C\mu}^{b}(m^2 g^{-1}_{C\mu})$	$D_{nCu}^{c}(nm)$
ZPS	_	_	<i>p_cw</i>
40Cu/ZPS	2.8	18.1	37.1
1Nb-40Cu/ZPS	2.7	17.4	38.7
2Nb-40Cu/ZPS	3.1	20.1	33.8
3Nb-40Cu/ZPS	3.3	21.0	32.0
4Nb-40Cu/ZPS	3.4	22.1	30.5
6Nb-40Cu/ZPS	3.5	22.4	30.0
4Nb-40Cu/ZPS-S ^d	3.2	20.9	28.9

^aDispersion of Cu NPs ^bSurface area of Cu NPs ^cSize of Cu NPs ^dSpent catalyst after five consecutive runs

Catalyst	Acidity by strength (mmol g ⁻¹)				<i>L/B</i> ratio	H_2 uptake (mmol g ⁻¹)	
	Weak	Medium	Strong	Total			
ZPS	0.42	0.08	0.37	0.88	N.A. ^b	0.060	
40Cu/ZPS	0.38	0.10	0.35	0.83	N.A.	5.460	
1Nb-40Cu/ZPS	0.38	0.09	0.40	0.87	3.91	5.680	
2Nb-40Cu/ZPS	0.39	0.08	0.44	0.92	4.21	5.790	
3Nb-40Cu/ZPS	0.37	0.11	0.49	0.96	4.60	5.880	
4Nb-40Cu/ZPS	0.38	0.11	0.53	1.03	5.38	6.180	
6Nb-40Cu/ZPS	0.39	0.15	0.53	1.08	5.78	6.010	
4Nb-40Cu/ZPS-S ^a	0.35	0.12	0.58	1.05	N.A.	6.020	

Table 3 Acidic properties of monometallic Cu/ZPS and bimetallic Nb-Cu/ZPS catalysts, as determined

using NH₃-TPD and Py-FTIR

^aSpent catalyst after five consecutive runs ^bNot available

Entry	Catalyst	X _{LA} ^b (%)	$S_{ m GVL}^{\ c}$	$S_{\rm VA}{}^{\rm c}$	$S_{\rm others}^{\rm c,e}$	Y _{GVL} ^d (mol%)	Y _{VA} ^d (mol%)	Y _{others} d,e
1	Blank	5.0	10.0	0	90.0	0.5	0	4.5
2	ZPS	25.9	76.4	0	23.5	19.8	0	6.1
3	10Cu/ZPS	50.2	89.6	0	10.3	45.0	0	5.2
4	20Cu/ZPS	62.7	89.9	0	10.0	56.4	0	6.3
5	30Cu/ZPS	71.4	90.2	0	9.8	64.4	0	7.0
6	40Cu/ZPS	80.3	94.3	0	5.6	75.8	0	4.5
7	50Cu/ZPS	78.9	90.7	0	9.2	71.6	0	7.3
8	1Nb-40Cu/ZPS	81.5	71.1	25.7	3.1	58.0	21.0	2.5
9	2Nb-40Cu/ZPS	88.4	40.3	57.2	2.3	35.7	50.6	2.1
10	3Nb-40Cu/ZPS	92.0	20.8	77.7	1.4	19.2	71.5	1.3
11	4Nb-40Cu/ZPS	95.6	2.3	96.7	0.9	2.2	92.5	0.9
12	6Nb-40Cu/ZPS	94.5	2.1	95.3	2.5	2.0	90.1	2.4
13	4Nb/ZPS	26.7	80.9	0	19.1	21.6	0	5.1
14	4Nb-40Cu/ZPS ^f	96.1	2.0	97.3	0.7	1.9	93.5	0.7

Table 4 Comparison of LA conversion and product selectivity using different types of catalysts^a

^aReaction conditions: 3.4 mmol of LA, 0.05 g of catalyst, 30 mL of H₂O, 150 °C, initial H₂ pressure of 3 MPa, 2 h

^bConversion of LA

^cSelectivity

dYield

eCalculated by subtracting 100 from S_{GVL} and S_{VA}

 ${}^{\rm f}\!\alpha\text{-}AL$ used as a feed stock

*3-PEA calculated in others



Scheme 1 Reaction pathway for conversion of glucose to valeric acid and valeric esters.



Fig. 1 Potential applications of VA in various chemical and fuel industries.

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Fig. 2 (a)–(b) XRD patterns of PS and ZPS supports, monometallic Cu/ZPS, and bimetallic Nb-Cu/ZPS catalysts. (b) FT-IR spectra of PS and ZPS. (c) N₂ adsorption–desorption isotherms and (c) BJH pore size distributions of ZPS support, monometallic Cu/ZPS, and bimetallic Nb-Cu/ZPS catalysts.



Fig. 3 HR-TEM and **HAADF-**STEM images of (a) ZPS, (b) monometallic 4Nb/ZPS, (c) monometallic 40Cu/ZPS, and (d) bimetallic 4Nb-40Cu/ZPS. (e) Schematic illustration of effect of Nb doping on morphology of Cu NPs.

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Fig. 4 Deconvoluted XPS core-level spectra of bimetallic Nb-Cu/ZPS catalysts: (a) Zr 3d core level peaks, (b) Cu 2p core level peak, and (c) Nb 3d core level peaks.



Fig. 5 (a) NH₃–TPD, (b) Py–FTIR, and (c) H₂–TPR profiles of ZPS, monometallic Cu/ZPS, and bimetallic Nb-Cu/ZPS, and (d) CO-DRIFT profile of 40Cu/ZPS and 4Nb-40Cu/ZPS.



Fig. 6 Arrhenius plots for (a) LA conversion and (b) VA selectivity. (c) TOF of bimetallic Nb-Cu/ZPS catalysts. 4Nb-40Cu/ZPS-S was the spent catalyst recovered from the reaction at 3.4 mmol LA, 150 °C, 30 mL H₂O, 3 MPa initial H₂ pressure, 2 h.



Fig. 7 (a) Adsorption of LA, VA, and 2,5-HED in water over PS, ZPS, and the 4Nb-40Cu/ZPS catalysts. (b) Schematic representation of LA adsorption over zirconium site of 4Nb-40Cu/ZPS catalyst *via* carboxylic acid group, followed by hydrogenation of ketone group to form 4-hydroxypentanoic acid (4-HPA).



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Fig. 8 LA conversion and product yield achieved over the 4Nb-40Cu/ZPS catalyst at (a) varying temperatures, using 0.05 g catalyst, 3.4 mmol of LA, 30 mL H₂O, and 3 MPa initial H₂ pressure for 2 h; (b) varying times, using 0.05 g catalyst, 3.4 mmol of LA, 150 °C, 30 mL H₂O, and 3 MPa initial H₂ pressure; (c) varying pressures, using 0.05 g catalyst, 3.4 mmol of LA, 150 °C, 30 mL H₂O for 2 h, (d) varying catalyst-to-feed ratios at 150 °C, 30 mL H₂O, and 3 MPa initial H₂ pressure for 2 h, and (e) varying LA concentration using 0.05 g catalyst, 150 °C, 30 mL H₂O, and 3 MPa initial H₂ pressure.



Fig. 9 LA conversion and product yield in various media over (a) bimetallic 4Nb-40Cu/ZPS catalyst and (b) monometallic 40Cu/ZPS catalyst. (c) Cyclic voltammetry profiles of various materials (Cu NPs, 8Nb92Cu, 40Cu/ZPS, and 4Nb-40Cu/ZPS) as the working electrode. Reaction conditions: 3.4 mmol LA, 30 mL H₂O, 3 MPa initial H₂ pressure, 150 °C, 2 h.

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Scheme 2 Plausible reaction pathway for the direct conversion of LA to VA over bimetallic Nb-Cu/ZPS catalyst.

Fig. 10 (a) Reusability of 4Nb-40Cu/ZPS catalyst in the conversion of LA. (b) XRD patterns of fresh, spent, and re-activated catalyst. (c) TGA profiles and (d)–(e) SEM and TEM images of fresh and spent catalysts. (f) Elemental mapping of spent catalyst. (h) ICP–OES of fresh and spent catalyst. (g) Schematic representation of effect of Nb promoter on leaching of Cu NPs (inset: image of product immediately after the reaction). Reaction conditions: 3.4 mmol of LA, 0.05 g of catalyst, 30 mL H₂O, 150 °C, initial H₂ pressure of 3 MPa, 2 h.

