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1. Introduction

With the rapidly depleting reserves of fossil fuels and its impact on global warming, more researchers are encouraged to focus on clean and sustainable resources to produce fuels and chemicals.^{1–3} Biomass is the most promising carbon feedstock due to its abundance and low cost. Among various biomass resources, lignocellulose, consisting of cellulose, hemicellulose

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Catalytic transfer hydrogenation of ethyl levulinate to γ -valerolactone over supported MoS₂ catalysts†

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The hydrogenation of levulinate esters to γ -valerolactone (GVL) is an important step in the transformation of biomass into biofuels. It is attractive to develop new efficient systems for the catalytic transfer hydrogenation (CTH) of levulinate esters to value-added GVL. In this work, a series of MoS₂-based supported catalysts were prepared *via* an impregnation method for the CTH of biomass-derived ethyl levulinate (EL) to GVL. By comprehensive characterization and catalytic measurements, we found that the CTH activity of EL to GVL is closely related to the MoS₂ morphology and acid distribution on the support. Among the catalysts with different supports, the AC support with abundant Lewis acid sites and large surface area facilitated the high dispersion of low stacked MoS₂ slabs, and the MoS₂-acid synergistic catalysis contributed to the superior activity and selectivity. The conversion of EL and the selectivity of GVL reached 97.2% and 91.2% under optimized conditions over the MoS₂/AC catalyst (230 °C, 1 MPa H₂, 1.5 h), respectively. We also conducted reaction kinetic experiments to reveal the relationship between the active site of the MoS₂/AC catalyst and its catalytic performance, and the plausible reaction pathway and mechanism over MoS₂/AC was proposed. The catalytic performance gradually declined during recycling tests due to the oxidation of MoS₂ and can be easily recovered by resulfuration.

> and lignin, has been the major subject for producing all sorts of molecules. Lignocellulose can be converted to platform chemicals and biofuels through the sugar platform or thermochemical platform.^{4,5} One of the most attractive biomass platform chemicals is GVL, which attracted considerable attention owing to its unique physical and chemical properties. For instance, GVL was deemed as a green organic solvent in the pretreatment of lignocellulose biomass.⁶ Additionally, GVL can be extensively utilized as a fuel additive suitable for petrol and diesel to enhance the fuel combustion process.^{3,7} Moreover, GVL was used as an important intermediate to produce high value-added chemicals like 2-methyl tetrahydrofuran and valerate esters, *etc.*⁸

> To date, many processes have been developed for the production of GVL from LA or its ester through hydrogenation reaction, where they can be directly produced from cellulose with high yields in ethanol solutions.^{9–12} Compared with LA, EL is much easier and more energy-efficient to be separated from the alcoholic mixture than the separation of LA from water. Therefore, it is attractive to develop efficient systems for the catalytic hydrogenation of EL to GVL.

Generally, according to the diversity of hydrogen sources, three major strategies have been explored for GVL production from EL, including H_2 , HCOOH and alcohol H-donor

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[†] Electronic supplementary information (ESI) available: XRD patterns of the AC support and MoS₂/AC catalysts with different Mo loadings; nitrogen adsorption-desorption isotherms of the AC support and MoS₂/AC catalysts with different Mo loadings; effects of the catalyst dosage on the conversion of EL into GVL; effects of the Co/Ni doping on the conversion of EL into GVL over the MoS₂/AC catalyst; XRD patterns of Co-MoS₂ (Co/(Co + Mo) = 0.45) and Ni-MoS₂ (Ni/(Ni + Mo) = 0.45); XPS spectra of Co-MoS₂/AC (Co/(Co + Mo) = 0.45) and Ni-MoS₂/AC (Ni/(Ni + Mo) = 0.45) catalysts; XPS spectra of the fresh and spent MoS₂/AC catalysts; textural properties of activated carbon and the MoS₂/AC catalysts. See DOI: 10.1039/d1cy00524c



(Scheme 1).¹³ However, both H₂ and HCOOH strategies have some limitations, such as harsh reaction conditions, use of corrosive acids, and use of precious metals and nonenvironmentally friendly solvents, which limited their further application.14 Fortunately, the CTH method based on the principle of Meerwein-Ponndorf-Verley (MPV) reduction for the hydrogenation of EL to GVL over heterogeneous catalysts using alcohols both as the H-donor and solvent was developed in recent decades. It is reported that the key step for the CTH reaction lies in the selective hydrogenation of EL to form 4-hydroxypentanoic acid (4-HPE),¹⁵ and an appropriate amount of acid can purge the dehydration and lactonization to further generate GVL.¹⁶ Therefore, many efforts have been devoted to designing efficient metal and metal oxide catalysts combined with acid supports for CTH of EL to GVL, including Ru, Pd, Ir, Ni, Cu, Co, CuO, ZrO₂, etc. (Scheme 1).¹⁷⁻¹⁹

Although metal and metal oxide catalysts showed good CTH activity with a rather high GVL yield (>90 °C) at a relatively low reaction temperature (<200 °C), the topic of developing new material has seldom been well addressed. To the best of our knowledge, besides metal and metal oxide catalysts, only a few studies have investigated the CTH activity of metal phosphides^{20,21} and metal-organic hybrids,^{13,22} let alone catalysts like metal carbide, nitride and sulfide. Thus, to achieve a new breakthrough in the CTH of EL to GVL, the development of improved catalytic systems and in-depth understanding of the reaction mechanism are necessary.

As aforementioned, the rational design of the catalyst focuses on the regulation of hydrogenation and dehydration ability. It has been reported that the MoS₂-based catalyst exhibited good activity in the hydrodesulfurization, hydrodenitrogenation and hydrodeoxygenation reaction, with the cleavage of the C=C and C-O (N/S) bond usually at high temperature (>250 °C) and high pressure (>3 Mpa H_2).^{23,24} The activity of MoS₂ has been linked to the availability of edge vacancy sites on the MoS₂ slabs, whereas coordinatively saturated sites on basal planes are regarded as catalytically inert.^{25,26} Moreover, the edge vacancy sites endow the catalyst with weak acid. To sum up, the MoS₂ catalyst possesses the following merits: economical, potential hydrogenation ability and weak acidity, which met the requirement of the active center for the CTH of EL to GVL.

Inspired by the special merits of MoS₂ materials, here we combined MoS₂ with various supports to adjust the hydrogenation and dehydration ability, aiming to achieve efficient production of GVL from biomass-derived levulinate esters (Scheme 1). To our knowledge, although disulfide catalysts like Mo and W have been widely used for the valorisation of biomass especially in the HDO of fats and lignin, the application of MoS₂-based catalysts in the CTH of LA and EL to GVL has not been reported in previous studies. Therefore, in this work, MoS₂-based supported catalysts were prepared via an impregnation method for the CTH of EL to produce GVL. The role of different supports (AC, Al₂O₃, SiO₂, TiO_2 , ZrO_2) was explored in the light of various characterization techniques, including XRD, N₂ physisorption, XPS, TEM, NH₃-TPD and Py-FTIR. Based on the characterization and catalytic measurements, the relationship between support properties, MoS₂ morphology, and catalytic performance was deeply discussed. We further investigated the effect of reaction conditions, different H-donors and substrates during the CTH reaction, and proposed a plausible reaction pathway and mechanism over MoS₂/AC. Moreover, the doping effect of Co or Ni on MoS₂/AC and the reusability of MoS₂/AC under optimal conditions were also investigated.

2. Experimental

2.1. Materials

Ammonium heptamolybdate $((NH_4)_6MO_7O_{24}\cdot 4H_2O),$ $Ni(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, methanol, ethanol, isopropanol, 1-butanol, 2-butanol, cyclohexane dodecane and 1,4-dioxane were provided by Tianjin Kemiou Chemical Reagent Co, Ltd. Ethyl levulinate (EL), levulinic acid (LA), methyl levulinate (ML), butyl levulinate (BL), cyclohexanone, γ -valerolactone (GVL), isopropyl levulinate (IPL) and isopropyl valerate (IPA) were bought from Aladdin. The above-mentioned chemicals were directly used without any pretreatments. Supports including AC (activated carbon), Al₂O₃, and SiO₂ were purchased from NORIT, Qingdao Haiyang Chemical Co. Ltd. and DICP, respectively. ZrO2 and TiO2 were purchased from Tianjin Kemiou Chemical Reagent Co, Ltd. The AC support was further treated with 50 vol% HNO3/H2O solution at 80 °C for 12 h to remove the small amount of SiO2. All the supports were dried at 400 °C in a N₂ flow for 4 h before use.

2.2. Catalyst preparation

All the supported MoS₂ catalysts were prepared using an incipient wetness impregnation method. Before the impregnation, the support was vacuum dried at 120 °C for 12

h. In a typical procedure, the support was adequately dispersed in an aqueous solution containing a certain amount of $(NH_4)_{6}$ -Mo₇O₂₄·4H₂O at room temperature for 24 h. Then the sample was dried at 120 °C for 12 h. Subsequently, the sulfidation of the dried solid was conducted in a flow of 10% H₂S/H₂ at 400 °C for 4 h. Finally, the catalysts with 8 wt% Mo loading on different supports were obtained and denoted as: MoS₂/AC, MoS₂/Al₂O₃, MoS₂/SiO₂, MoS₂/TiO₂, and MoS₂/ZrO₂. The MoS₂/ AC catalysts with different Mo loadings were denoted as: $xMoS_2/AC$, where x represents the Mo loading.

The contrast sample MoO₃/AC was obtained *via* the direct calcination of the impregnated precursor at 400 °C for 4 h in air. The unsupported MoS₂ was synthesized by the sulfidation of MoO₃ derived from the decomposition of $(NH_4)_6MO_7$ -O₂₄·4H₂O. The sulfidation of the AC and Al₂O₃ support in the absence of Mo loading was also conducted to obtain sulfurated supports, denoted as AC–S and Al₂O₃–S.

A series of supported Co- or Ni-doped MoS₂/AC catalysts were prepared by varying the Co/(Co + Mo) or Ni/(Ni + Mo) molar ratio in the range of 0, 0.25, 0.45, and 0.62, while maintaining the Mo loading at 8 wt%. The preparation process and treatment conditions were the same as those of MoS₂/AC with the addition of Co(NO₃)₂·6H₂O or Ni(NO₃)₂·6H₂O in the precipitation step.

2.3. Catalyst characterization

The X-ray powder diffraction (XRD) patterns were recorded on a D8-Focus powder diffractometer, using Cu-K α radiation at 40 kV and 200 mA in the range of 10° to 80° at a scanning speed of 5° min⁻¹.

The Brunauer–Emmett–Teller (BET) method was used to calculate the specific area of the mesoporous materials with a Micromeritics TriStar surface area and porosity analyzer. The pore volume and pore size were obtained by the BJH method from the isotherms. Before the measurement, the catalysts were degassed at 300 °C for 3 h on a vacuum line.

Transmission electron microscopy (TEM) was performed using a JEM-2100F transmission electron microscope operated at 200 kV. Before the samples test, the catalysts were ultrasonicated with ethanol and dropped onto copper grids. The average length (\bar{L}) and stack number (\bar{N}) of the slabs and the edge-to-corner ratio of the MoS₂ slab $(f_e/f_c)_M$ were calculated using eqn (1)–(3), where n_i was the number of slabs in the unit and L_i and N_i were the length of the slab and the stacking number of the unit. The L_i and N_i were obtained by statistical analysis of more than 100 stacked MoS₂ units from different parts of each sample, which were analyzed with a program Digital Micrograph.

$$\tilde{L} = \sum_{i=1}^{n} n_i L_i / \sum_{i=1}^{n} n_i$$
(1)

$$\tilde{N} = \sum_{i=1}^{n} n_i N_i / \sum_{i=1}^{n} n_i$$
(2)

$$(f_{\rm e}/f_{\rm c})_{\rm M} = (10 \times \bar{L}/3.2 - 3)/2$$
 (3)

X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo Fisher ESCALABTM 250Xi spectrometer. Peak positions were calibrated by using a C 1s peak at 284.4 eV as a standard.

To examine the acidity of the catalysts, the temperatureprogrammed desorption of ammonia (NH₃-TPD) was performed on an AutoChem 2920 chemisorption analyzer. 0.1 g catalyst was pretreated with a flow (40 mL min⁻¹) of Ar at 600 °C for 1 h. After cooling down, the samples were saturated with NH₃. Subsequently, the temperature rose to 800 °C at a rate of 5° min⁻¹ and the desorption was monitored using a thermal conductivity detector (TCD). Fourier-transform infrared (FT-IR) spectra of adsorbed pyridine were recorded using a Tensor 27 (Bruker, Germany) spectrophotometer in the wavenumber range of 1400–1700 cm⁻¹, using KBr pellets, with a resolution of 4 cm⁻¹ at 32 scans. Typically, 6.0 mg of the catalyst was placed in a diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) cell $(1 \times 10^{-3} \text{ Pa})$ and heated to 400 °C in a N₂ flow for 2 h to obtain a relatively clean surface. The sample system was cooled down to room temperature and the background spectrum was recorded. Then, pyridine was introduced into the sample cell for 120 min to allow the adsorption equilibrium of pyridine. After the physically adsorbed pyridine was purged off under vacuum conditions, the evacuation was performed at 150 °C to measure the IR spectra. Quantitative analysis of the concentration of Brønsted and Lewis acid sites can be obtained using eqn (4) and (5), where $C_{\rm B}$ and IA_B represent the concentration of the Brønsted acid sites and the integrated absorbance peak at 1540 cm⁻¹ for the Brønsted acid sites. CL and IAL represent the concentration of the Lewis acid sites and the integrated absorbance peak at 1450 cm⁻¹ for the Lewis acid sites. *R* is the radius of the sample disc, and W is the weight of the sample.

$$C_{\rm B}(\mu {\rm mol g}^{-1}) = (1.88 \times {\rm IA}_{\rm B} \times R^2)/W \tag{4}$$

$$C_{\rm L}(\mu \text{mol } \text{g}^{-1}) = (1.88 \times \text{IA}_{\rm L} \times \text{R}^2)/W \tag{5}$$

2.4. Catalyst test

Transfer hydrogenation of EL to GVL was performed in a 50 mL Parr reactor (Parr 4597). Typically, 2 mmol (0.2283 g) EL, 75 mg catalysts and 20 mL isopropanol were placed into the autoclave. After being purged three times, H2 was introduced into the autoclave to reach a certain pressure at ambient temperature. Then the reactor was heated up to a certain temperature and reacted for certain hours with stirring at 1000 rpm. When the reaction finished, the liquid products were extracted until they cooled down to room temperature. The obtained liquid products were directly identified by GC-MS (Agilent 6890A-5975C) and quantified by GC (SP-7890) using a flame ionization detector (FID) with a 30 m \times 0.25 mm × 0.25 µm WondaCap WAX capillary column. The experiments have been repeated at least twice to ensure the accuracy and rationality. The conversion of EL and the yield of GVL were calculated as follows.

$$Conversion = \left(1 - \frac{\text{molar of residual EL}}{\text{molar of initial EL}}\right) \times 100\% \quad (6)$$

Product yield =
$$\frac{\text{molar of GVL in the products}}{\text{molar of initial EL}} \times 100\%$$
 (7)

3. Results and discussion

3.1. Characterization of the catalysts

3.1.1 Composition and structure. To better understand the composition and structure of the supported MoS₂ catalysts, several characterization techniques were used to study their properties in detail. XRD was performed to identify the crystal structure of the catalysts, as shown in Fig. 1. The diffraction pattern of MoS₂ exhibits several specific peaks at 14.4°, 33.5°, 39.5° and 58.9°, corresponding to (002), (100), (103), and (110) (JCPDS 37-1492), respectively.^{27,28} It has been reported that the existence of the (002) planes indicated the formation of a multilayer MoS₂ structure.²⁷ However, hardly any characteristic peaks of MoS₂ including the (002) planes can be found for the as-prepared supported MoS₂ catalysts, indicating the low stacked layers as well as high dispersion of MoS₂ in the catalysts, which can be further confirmed by the following TEM results. Moreover, broad peaks of the (100) and (110) planes were observed in MoS_2/AC and $MoS_2/$ Al₂O₃, while they were not found in MoS₂/ZrO₂, MoS₂/SiO₂ and MoS₂/TiO₂. This was probably because of the coverage of the high crystallinity degree of the latter three supports. For MoS₂/AC with an increased Mo loading from 5 wt% to 20 wt%, the intensity of the MoS2 diffraction peak corresponding to the (100) and (110) plane gradually increased, while the (002) plane still was not observed (Fig.



Fig. 1 XRD patterns of the ${\sf MoS}_2$ catalysts with different supports (8 wt% Mo loading).

S1[†]). This indicates that the enhancement of Mo loading on the AC support was favorable for the oriented growth of the (100) and (110) plane of MoS_2 slabs.

TEM characterization was carried out to further observe the microstructure and metal dispersion of the catalyst, as shown in Fig. 2. The calculated space between two parallel dark thread-like fringes was about 6.4 Å, corresponding to the (002) basal planes of the hexagonal MoS₂ material.^{29,30} As shown in Table 1, it was estimated that the mean slab length for MoS₂/AC, MoS₂/Al₂O₃, MoS₂/SiO₂, MoS₂/TiO₂ and MoS₂/ ZrO₂ was 4.6 nm, 4.8 nm, 5.0 nm, 4.5 nm and 5.2 nm, respectively. The edge-to-corner ratio of the MoS₂ slab was calculated according to the literature and was regarded as evidence of the relative amount of the MoS₂ edge active site.³¹ It seems that no apparent distinction of the edge-tocorner ratio was found for the supported MoS₂ catalysts. However, a significant difference was found for the stacked layers of MoS₂. In particular for MoS₂/AC, highly dispersed low stacked MoS_2 slabs (~1.4 layers) on the support were observed, which has been proved to be more active in the HDO reaction.^{32,33} According to the STEM mapping images of the samples, Mo and S were well dispersed on the supports. In summary, the MoS₂ slabs on different supports displayed significant effects on the stacked layers, which should greatly affect the catalytic activity.

3.1.2 Porosity characteristics. N_2 physisorption measurement was performed to investigate the porous properties of the samples. Fig. S2[†] shows the adsorptiondesorption isotherms of the AC support and MoS₂/AC catalysts with different Mo loadings. The observed noticeable hysteresis revealed the presence of the mesoporous nature in the catalysts. The Brunauer-Emmett-Teller surface area (S_{BET}) , pore volume and pore size data of the MoS₂-based supported catalysts are summarized in Table 2. Among the catalysts, MoS₂/AC possessed a quite larger BET surface area when compared to other supports, which is proved to be beneficial for the mass transfer and the contact between the reactants and the active sites.^{33,34} After the impregnation of MoS₂ on AC, the specific surface area decreased from 1161 to 507 $m^2 g^{-1}$ and the pore volume decreased from 0.39 to 0.21 $\mbox{cm}^3\ \mbox{g}^{-1}$ with the Mo loading increasing from 0 to 20 wt% (Table $S1^{\dagger}$). It is proposed that the impregnation of MoS_2 may result in the blockage of pores of the support, which is ascribed to the so-called dilution effect.35

3.1.3 Surface species of the catalysts. Considering that dehydration/cyclization on acid sites was presumably involved in the hydrogenation of EL to GVL,^{36,37} the acidic properties of MoS_2 -based supported catalysts were investigated by using temperature-programmed desorption of NH_3 (NH_3 -TPD) and IR spectroscopy of pyridine adsorption. Without regard to the bare acidity of MoS_2 itself, the main acidity of the samples should be provided by the supports. As shown in Fig. 3(a) and Table 2, $\text{MoS}_2/$ AC possessed the highest acid amount of 2054 µmol NH_3 per g cat with two desorption peaks at 271.8 °C and 711.4 °C, which belonged to weak and strong acid sites,





 $\label{eq:Fig.2} Fig. 2 \quad \text{TEM images and STEM mapping of (A) } MoS_2/AC, (B) \\ MoS_2/Al_2O_3, (C) \\ MoS_2/SiO_2, (D) \\ MoS_2/TiO_2, \\ \text{and (E) } MoS_2/ZrO_2. \\ \text{TEM images and STEM mapping of (A) } MoS_2/AC, \\ \text{TEM images and STEM mapping of (A) } MOS_2/$

Table 1	Morphological charac	teristics of the MoS ₂ a	active phase species	calculated from H	IRTEM micrographs (8	wt% Mo loading)
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Entry	Catalysts	Average length L (nm)	Average stacking number \bar{N}	$(f_{\rm e}/f_{\rm c})_{\rm M}{}^a$
1	MoS ₂ /AC	4.6	1.4	5.7
2	MoS_2/Al_2O_3	4.8	2.6	6
3	MoS ₂ /SiO ₂	5.0	4.1	6.3
4	MoS ₂ /TiO ₂	4.5	3.1	5.5
5	MoS_2/ZrO_2	5.2	3.6	6.6

^{*a*} Calculated from HRTEM data. The edge-to-corner ratio of the MoS₂ slab $(f_c/f_c)_M$ was derived according to eqn (1)–(3).

respectively. It was reported that the acid-pretreatment of AC would introduce abundant oxygen-containing functional

groups on the surface, which can act as the acid site. 38 For $MoS_2/Al_2O_3,\ strong$ acid sites located at 507.7 oC were

Table 2 Textural properties and surface acidity of the supported MoS₂ catalyst (8 wt% Mo loading)

Entry	Sample	$S_{\rm BET}^{\ \ a} ({\rm m}^2 {\rm g}^{-1})$	Pore volume ^{b} (cm ³ g ⁻¹)	Pore size ^{b} (nm)	Acidity ^c (μ mol NH ₃ per g cat.)
1	MoS ₂ /AC	763	0.31	3.9	2054
2	MoS ₂ /Al ₂ O ₃	101	0.17	4.3	1498
3	MoS_2/ZrO_2	118	0.29	6.2	312
4	MoS ₂ /SiO ₂	371	0.53	4.4	78
5	MoS_2/TiO_2	64	0.27	16.4	180

^a BET surface area. ^b Average pore volume and size were calculated by the BJH method from desorption branches. ^c Calculated by NH₃-TPD.



observed and its total acid amount was 1498 µmol NH3 per g cat. MoS₂/TiO₂ and MoS₂/ZrO₂ display apparent lower acidity with the total acid amount of 180 and 312 µmol NH_3 per g cat, respectively. It's worth noting that MoS_2/SiO_2 also exhibited weak acidity with the total acid amount of 78 µmol NH₃ per g cat. As both MoS₂/AC and MoS₂/Al₂O₃ possessed strong acidity, the Py-FTIR was performed to further analyze the acidic character of the catalyst, as shown in Fig. 3(b). For MoS₂/AC, the peaks at 1490, 1540, and 1640 cm⁻¹ were pyridine-adsorbed Brønsted acid sites including S-OH and surface -OH, while the pyridine-adsorbed Lewis acid sites consisting of Mo species and surface O-contained group showed peaks at 1450, 1490, and 1610 cm^{-1.39} For MoS₂/Al₂O₃, the Al₂O₃ support provides Brønsted acid sites from the Al-OH-Al group and Lewis acid sites from the Al center. Quantitative results (Table 3) showed that both the AC and Al₂O₃ support mainly provided Lewis acid sites, and the calculated ratios between the B-acid and L-acid were not more than 0.15.

In order to investigate the chemical state of Mo and S in the supported MoS₂ catalysts, X-ray photoelectron spectroscopy (XPS) was carried out. As shown in Fig. 4(a), four peaks are observed in the high-resolution XPS spectra of Mo 3d-S 2s, where the one at 226.9 eV corresponds to S 2s of MoS₂.⁴⁰ The two main peaks at 229.6 and 232.8 eV can be assigned to the Mo⁴⁺ ions in MoS₂ while the high binding energy at 233.1 eV and 236.2 eV can correspond to Mo⁶⁺ in MoO₃. For S 2p spectra shown in Fig. 4(b), two peaks at 162.5 eV and 163.9 eV were assigned to the S $2p_{3/2}$ and S $2p_{1/2}$ of divalent sulfide ions (S^{2-}). The higher binding energy S $2p_{3/2}$ peak at 163.5 eV and S $2p_{1/2}$ peak at 163.5 eV and the S $2p_{3/2}$ peak at 164.7 eV were due to monovalent sulfide ions $(S_2^{2^{-}})$. In addition, a broad peak at 169.0 eV representing the SO_x group was also observed. It can be clearly seen that most of the surface Mo species existed as MoS₂, indicating the formation of MoS₂ nanoparticles on the supports. Besides, it is observed that the catalysts with strong acidity displayed a high Mo^{6+}/Mo^{4+} ratio and SO_x proportion. This was probably

able 3 Pyridine-FTIR surface acid sites of the MoS ₂ /AC and MoS ₂ /Al ₂ O ₃ samples								
Catalysts	Brønsted acid sites (μ mol g ⁻¹)	Lewis acid sites ($\mu mol g^{-1}$)	Total acid sites (μ mol g ⁻¹)	$\rm B/L$				
MoS ₂ /AC	73.3	6.7	80.0	0.091				
MoS ₂ /Al ₂ O ₃	34.9	4.7	39.6	0.135				

Paper



due to the adsorption of H_2S species on the acid sites suppressing the proceeding of the vulcanization reaction during the sulfidation process.

3.2. Catalytic performance and discussion

The catalytic activities of the catalysts were tested by CTH of EL at 230 °C under 1 MPa H_2 for 1.5 h. As shown in Table 4,

 MoS_2 -based catalysts with different supports demonstrated significant differences in activity. A negligible reaction occurred in the blank experiment, indicating that carbonyl groups were thermally stable at 230 °C (entry 1). When the bulk unsupported MoS_2 was added, the EL conversion and GVL yield rose to 51.4% and 28.5%, respectively (entry 2). This indicates that the intrinsic hydrogenation ability derived from the edge site of MoS_2 can availably catalyze the CTH of

Table 4 CTH	able 4 CTH of EL to GVL with various catalysts ^a								
		Catalyst)=° + ~			· ``			
	EL	GV	νL	IPL	IPA				
			Yield (%)						
Entry	Catalyst	Conv. (%)	GVL	IPL	IPA	GVL Sel. (%)			
1	Blank	4.8	0.2	4.5		4.2			
2	MoS_2	51.4	28.5	18.8	1.4	55.4			
3	AC	44.8	31.9	10.0	_	71.2			
4	Al_2O_3	52.8	30.2	18.2	1.4	59.4			
5	ZrO_2	44.5	32.6	4.8	0.8	73.2			
6	SiO_2	15.6	8.2	10.8	—	52.6			
7	TiO ₂	51.7	27.8	18.9	1.3	53.6			
8	AC-S	42.8	32.2	9.1	_	75.2			
9	MoS_2/AC	97.2	88.7	0.3	2.0	91.2			
10	Al ₂ O ₃ –S	51.3	31.4	17.6	1.6	61.2			
11	MoS ₂ /Al ₂ O ₃	95.8	78.3	4.0	5.2	81.7			
12	MoS_2/ZrO_2	61.8	48.9	8.7	1.3	78.9			
13	MoS_2/SiO_2	17.0	12.7	2.3	1.6	74.7			
14	MoS ₂ /TiO ₂	58.3	44.7	0.2	1.2	76.7			

^a Reaction conditions: 2.0 mmol EL, 75 mg catalyst, 20 mL isopropanol, reaction temperature 230 °C, initial H₂ pressure 1 MPa, reaction time 1.5 h,

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EL. However, for the bulk MoS₂, its edge site amount was relatively low and limited its activity. Thus, it is necessary to introduce an appropriate support to realize the enhancement of exposed MoS₂ edge sites. Then, the function of various supports with different structures and surface acidity were discussed. For single supports without MoS₂ loading (entries 3-7), as we expected, a relatively low EL conversion and GVL yield were observed due to the absence of robust hydrogenation sites. As mentioned above, the dehydration/ cyclization on acid sites was presumably involved in the hydrogenation of EL to GVL, and the displayed activity for the single supports mainly comes from their surface acid center. Therefore, it can be seen that the AC, Al₂O₃, ZrO₂, and TiO₂ supports with relatively higher acidity showed higher activity with a GVL yield around 30%, whereas the SiO₂ support with a very small number of acid sites only achieved an 8.2% yield of GVL. Moreover, the XPS results have indicated the formation of SO_x species on the supported MoS₂ samples, which are easily converted to strongly acidic "sulfuric acid" in the presence of water vapor. To eliminate the influence of the surface SO_x species, the catalytic activity of the sulfurated AC and Al₂O₃ support was also investigated. As shown in entry 8 and entry 10, there is nearly no difference between the un- and sulfurated support. When MoS₂ was impregnated on the supports, no obvious improvement was observed for MoS₂/SiO₂, MoS₂/ZrO₂ and MoS_2/TiO_2 (entries 12-14). It can be seen that the EL conversion only increased slightly while the GVL selectivity increased more remarkably. However, for MoS₂/AC and MoS₂/ Al_2O_3 (entry 9 and entry 11), significant enhancement was found with the impregnation of MoS_2 on the support. $MoS_2/$ AC presented a 97.2% EL conversion and 91.2% GVL selectivity, while MoS₂/Al₂O₃ exhibited a 95.8% EL conversion and 81.7% GVL selectivity.

Many factors can affect the catalytic activity such as particle size, dispersion, acid properties, chemical properties, etc.41 In our case, it seems that the acidity of the support mainly influences the catalytic activity of the supported MoS₂ catalysts. The catalyst with high acidity achieved relatively high activity, according to the catalytic performance and the NH₃-TPD results. Garcia et al.42 demonstrated that strong metalsupport interactions occurred with the Mo precursor interacting mainly with Lewis acid sites, and this stage has a key effect on the genesis of the sulfide phase, and can strongly change the morphology, activity and selectivity of the resulting MoS₂ slabs. Thus, although the AC, Al₂O₃, ZrO₂, and TiO₂ supports showed similar activity, their distinct difference in the acid content significantly affects the MoS₂ morphology, which directly determines the hydrogenation ability of the catalyst. According to the TEM analysis, the MoS₂ slabs on different supports displayed significant effects on the stacked layers. As a consequence, the AC and Al₂O₃ support with abundant Lewis-acid sites facilitated the formation of low stacked MoS₂ slabs, and significant activity enhancement was found with the impregnation of MoS₂ on the AC and Al₂O₃ support. This indicates that the surface acid site on the support not only catalyzed the CTH reaction but also significantly affected the MoS_2 morphology. Moreover, the overwhelmingly larger surface area of the AC support may also contribute to the high dispersion of MoS_2 slabs and was beneficial for mass transfer in the catalytic process. In conclusion, the AC support with abundant Lewis acid sites and large surface area facilitated the high dispersion of low stacked MoS_2 slabs, and the MoS_2 -acid synergistic catalysis contributes to the superior activity and selectivity in CTH of EL to GVL.^{37,43,44}

3.3. Study of the reaction mechanism

We conducted reaction kinetic experiments to reveal the relationship between the active site of the MoS_2/AC catalyst and its catalytic performance. The details are as follows.

3.3.1 Optimization of reaction conditions. The reaction temperature can affect the temperature dramatically. Therefore, a variety of experiments were carried out at different temperatures viz. 210, 220, 230, 240 and 250 °C. As shown in Fig. 5(a), a low-temperature limits the catalyst activity and increasing the temperature effectively enhanced the EL conversion and GVL yield. When the temperature increased to 230 °C, EL was almost completely converted and the yield of GVL could reach up to 88.7%. However, when the temperature increased above 230 °C, the GVL yield decreased remarkably. It was not surprising that a higher temperature could improve the catalytic activity and the reaction rate. However, the intrinsic activity of MoS₂ for further C-O cleavage and oxygen removal will be promoted under excessive temperature conditions,45 which led to the decline of GVL production.

The effect of hydrogen pressure was also studied, and the catalyst activity is shown in Fig. 5(b). Without external H_2 added into the system, the EL conversion and GVL yield was relatively low. Although isopropanol acted as the H-donor as well as solvent in the CTH of EL, the sulfur vacancies on the edge site of MoS_2 can hardly be created in the single function of the H-donor. Therefore, the addition of external H_2 could help to the formation of sulfur vacancies of the catalyst termed as coordinatively unsaturated sites, which served as active sites for the CTH reaction. It was found that the optimized hydrogen pressure is 1 MPa; a lower or higher hydrogen pressure would cause incomplete reaction or a decline of GVL production.

The influence of reaction time over MOS_2/AC was investigated to understand the reaction process (Fig. 5(c)). In the first 0.5 h, the EL conversion reached 82.8% and the GVL yield achieved 78.1%. Trace intermediates were detected as IPL, IPA, and other over-hydrogenated by-products derived from GVL (not quantitative). With the extension of reaction time, the yield of GVL increased first and reached the highest in 1.5 h, and then decreased gradually. Meanwhile, IPL gradually disappeared *via* the CTH reaction like EL. A small amount of IPA was maintained throughout the entire reaction and other over-hydrogenated by-products derived from GVL were markedly increased after 1.5 h. This indicates that GVL



Fig. 5 Effects of the reaction conditions on the conversion of EL into GVL over the MoS_2/AC catalyst. Reaction conditions: EL 2 mmol, catalyst 75 mg, isopropanol 20 mL. (a) Effect of reaction temperature, 1.5 h, 1 MPa H₂; 8 wt% Mo loading. (b) Effect of initial H₂ pressure, 230 °C, 1.5 h, 8 wt% Mo loading. (c) Effect of reaction time, 230 °C, 1 MPa H₂, 8 wt% Mo loading. (d) Effect of Mo loading, 230 °C, 1.5 h, 1 MPa H₂.

was not the terminal product in this catalytic system and it will further transform into a down-stream product.

The effect of the MoS_2/AC catalyst dosage on the conversion of EL into GVL in isopropanol at 230 °C with 1.5 h was investigated and the results are shown in Fig. S3.† With the increase of the catalyst dosage, the trend of the conversion results was similar to that of the reaction temperature and hydrogen pressure. The products detected by GC-MS indicated that more catalyst dosage resulted in excessive hydrogenation of GVL. It is obvious that the amount of the MoS_2 edge active site, as well as the acidity, will increase with the enhancement of the catalyst dosage, which will lead to an improvement in the excessive hydrogenation of GVL.⁴⁶

We further explore the effect of Mo loadings on the CTH reaction. As shown in Fig. 5(d), when adding 5 wt% of Mo on the AC support, both the conversion and yield increased remarkably. With the Mo loading increasing to 8 wt%, the highest EL conversion and product selectivity were achieved. However, a further increase in the weight percentage of the Mo element led to a slight reduction in the selectivity towards GVL. For the 20% MoS₂/AC catalyst, 84.4% yield of GVL was obtained at 97.2% conversion of EL, indicating that more by-products were produced. Similar to the conclusion on the effect of the catalyst dosage, excessive amounts of MoS₂ edge sites as well as acidity sites will promote excessive hydrogenation of GVL.

3.3.2 Effect of hydrogen donors. In the CTH of LA and its esters, the conversion of the reactant and the yield of GVL

were significantly related to the readiness of deriving the active H atom from the hydrogen donor. Thus, a variety of protic solvents (such as methanol, ethanol, isopropanol, 1-butanol, and 2-butanol) and aprotic solvents (such as cyclohexane and 1,4-dioxane) were used to study their effectiveness in the CTH of EL. As shown in Table 5, the solvent significantly affects the EL conversion and GVL selectivity under the optimized conditions. When cyclohexane and 1,4-dioxane were used, EL was basically not converted and little GVL was obtained. Although the addition of H₂ could activate the formation of sulfur vacancies of MoS₂, the hydrogenation of EL to 4-HPE can hardly occur in the absence of a H-donor, which further confirmed that the MoS₂-catalyzed conversion of EL to GVL completely follows the MPV route. Deservedly, when various alcohols served as the solvent, higher EL conversion and GVL yield were achieved. Notably, different alcohols with discriminative H donor capability demonstrated significant differences in activity. It's difficult for primary and tertiary alcohols to provide H-movement.15,47 As a result, the CTH reaction with methanol or 1-butanol as a solvent achieved a high EL conversion but a relatively low GVL selectivity. It is obvious that when the secondary alcohol was utilized, the GVL selectivity was much higher because of their active β -H movement.48 For example, EL was almost converted completely and the yield of GVL was 88.7% when isopropanol was used as a solvent. When further increasing the alkyl chains of secondary alcohol, the production of GVL significantly decreased (2-butanol). We speculated that it is the enhancive space steric effect of 2-butanol inhibits the hydrogen transfer reaction.⁴⁹ In conclusion, EL can be condensed in different alcohol solvents to produce GVL, and we believe that isopropanol as a hydrogen donor is worthy of further research in our system in terms of its reactivity as well as the practical point of view. These results further highlight that the effective transformation of EL to GVL over MoS₂/AC catalyst follows the MPV route since the hydrogen supply capacity of the solvent plays a vital role.

3.3.3 Effect of Co/Ni doping. Previous experimental and theoretical studies pointed out that Co or Ni doping will increase the availability of vacancy sites by lowering the Mo–S bond energy, and the formation of the CoMoS or NiMoS phase presented enhanced activity in HDO, HDS and HDN reactions.^{50–52} Therefore, we further investigated the effects of Co/Ni doping on the conversion of EL into GVL over the MoS₂/AC catalyst, and the results are shown in Fig. S3.[†] However, the Co–MoS₂/AC and Ni–MoS₂/AC catalysts with different doping contents present unexpectedly lower EL conversion and GVL yield when compared to the MoS₂/AC catalyst. The XRD and TEM analysis demonstrated the formation of MoS₂ slabs and their high dispersion on the AC support (Fig. S5 and S6[†]), and the XPS results showed that Ni(Co) mainly existed as Ni(Co)²⁺ in the Ni(Co)–S bond (Fig.

Table 5 The	Table 5 The effect of different solvents on the hydrogenation of EL to GVL						
Entry	Solvent		Conv. (%)	Yield (%)	Sel. (%)		
1	Methanol		81.1	22.2	27.3		
2	Ethanol		72.8	50.9	69.9		
3	Isopropanol		97.2	88.7	91.2		
4	1-Butanol		78.4	46.0	58.7		
5	2-Butanol		87.7	67.1	76.5		
6	Cyclohexane		18.2	9.4	51.6		
7	1,4-Dioxane		1.6	0.6	37.5		

Reaction conditions: EL 2 mmol, 8 wt% MoS_2/AC 75 mg, solvent 20 mL, 230 °C, 1.5 h, 1 MPa H₂.

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S7†).²³ Moreover, it is obvious that Ni(Co) doping leads to a lower sulfuration degree of the Mo species. This probably explained why these bimetallic Co(Ni)–MoS₂/AC catalysts are less effective than the monometallic MoS₂/AC catalyst.

3.3.4 Effect of substrates. In order to verify the versatility of the catalyst and better understand the reaction mechanism during the MoS₂/AC catalyzed CTH reaction, several biomassderived carbonyl compounds were evaluated as substrates under optimum reaction conditions. As shown in Table 6, it can be observed that the C=O group in aldehydes and ketones can be selectively hydrogenated to -C-OH with high conversion (>90.0%) and high selectivity (>88.0%) (entries 1-3). This clearly indicates that EL was firstly transformed into 4-HPE in the CTH reaction of EL to GVL, although no 4-HPE was detected during the reaction because it can quickly convert to GVL via internal esterification. In addition, the catalyst presented good performance in transforming different levulinate derivatives to GVL, including LA, methyl levulinate (ML) and butyl levulinate (BL). Notably, LA and ML were converted to GVL with the yield of 79.6% and 81.9%, respectively (entries 4 and 5). However, BL exhibited a relatively low activity probably due to the steric hindrance of butyl (entry 6). Above all, the MoS₂/AC catalyst revealed superior activity in the selective hydrogenation of the C=O group to -C-OH, and presented great potential for the CTH reactions of carbonyl compounds.

3.3.5 Reaction pathway and mechanism. On the basis of the qualitative analysis of GC-MS and the trend of product

distribution over time, we proposed a possible pathway for the EL to GVL reaction (Scheme 2) using the MoS_2/AC catalyst. Generally, EL was firstly converted to 4-HPE *via* the transfer hydrogenation. Subsequently, 4-HPE further underwent lactonization to form GVL. Besides, a couple of side reactions also happened in this system. EL will be converted to IPL *via* transfer hydrogenation like EL, and GVL will undergo excessive hydrogenation to form IPA, pentanoic acid, *etc.*

Based on previous research, Lewis acid sites has an important effect on the transfer hydrogenation reaction whereas Brønsted acid sites play an important role in the lactone reaction of 4-HPE.14,16 However, in this MoS₂/AC catalyzed system, the MoS₂ edge sites acted as the robust hydrogenation sites and the acid sites mainly promoted the lactone reaction of 4-HPE. Regarding previous studies^{13,53,54} and our previous results, we proposed a plausible explanation for the MPV reaction of EL to GVL over the MoS₂/AC catalyst, as shown in Scheme 3. In the presence of molecular H2 at high temperature, the S vacancies were generated on the edge of MoS₂, regarded as the active sites for the adsorption of EL and H-donor isopropanol.^{55,56} The Mo⁴⁺ and S²⁻ center interacted with both isopropanol and EL to form a six membered ring transition state. At this stage, the corresponding alkoxide generated from the dissociation of isopropanol readily transferred hydride ions to attack the carbonyl group of EL to yield 4-HPE. At the same time, isopropanol was converted into acetone with the loss of two

Entry	Substrates	Products	Conv. (%)	Yield (%)	Sel. (%)
1		OH	94.8	87.2	92.0
2		ОН	97.6	93.5	95.8
3		ОН	98.2	92.3	94.0
4	ОН		93.2	79.6	85.4
5			95.2	81.9	86.0
6			84.7	73.2	86.4

Reaction conditions: substrate 2 mmol, 8 wt% MoS₂/AC 75 mg, isopropanol 20 mL, 230 °C, 1.5 h, 1 MPa H₂.



hydrogen atoms. No detection of 4-HPE by GC analysis supported the fact that intramolecular transesterification of 4-HPE into GVL was very fast *via* the promotion of the surface acid site on the AC support, and the control step was located in the transfer hydrogenation of EL to 4-HPE. Therefore, the rational design of MoS_2 on the acid support to engineer highly dispersed low stacked MoS_2 slabs as the robust hydrogenation center was extremely important to achieve high activity in the CTH of EL to GVL.

The performance of the MoS_2/AC catalyst for the CTH of EL was also compared with those previously reported in the literature (Table 7). Although the MoS_2/AC catalyst presented comparable GVL yield with those reported in the literature, a relatively higher reaction temperature is non-negligible. It's worth noting that external H_2 is essential for the activation of MoS_2 to form sulfur vacancies as the active center, whereas it is needless for the metal catalyst or Zr-based solid catalyst. Hence, this MoS_2/AC catalyst perhaps provides a new idea for the CTH of EL to GVL to a certain extent, but there are indeed some obvious weaknesses to limit its applicability. Strategies such as the design of $Co-MoS_{2-x}$ metal-vacancies⁶¹ or MoS_2 monolayer sheets decorated with isolated Co atoms⁶² might be able to solve these problems.

3.4. Stability and reusability of the catalyst

The economic benefit is significant in the industrial production process, so the recyclability of the 8 wt% MoS_2/AC catalyst was tested under optimized reaction conditions. The catalyst was separated by filtration, washed with ethanol three times and subsequently dried for 2 h at 120 °C before next use. The results are shown in Fig. 6. The conversion of EL and yield of GVL gradually decreased after 4 runs. When comparing the spent catalyst with the MoO_3/AC catalyst, similar catalytic activity was observed. According to the literature,³² it may be the replacement of S with O species in the catalyst, which leads to the sulfur loss and the formation of Mo oxidized species.



Scheme 3 Plausible mechanism of the MPV route for CTH of EL to GVL over the MoS₂/AC catalyst.

Table 7	Comparison of the catalytic performance of MoS ₂ /AC with other catalysts in the CTH of EL to GV	/L
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Entry	Catalyst	H-Donor	T (°C)	P^a (Mpa)	<i>t</i> (h)	Conv. (%)	Yield (%)	Ref.
1	MOF-808	Isopropanol	130	_	3	100	85.0	13
2	Zr-HBA	Isopropanol	200	_	1	100	96.8	14
3	Cu-Ni/Al ₂ O ₃	2-BuOH	150	_	12	100	97.0	15
4	ZrFeO	Isopropanol	230	_	0.5	94.2	86.7	57
5	CuNi/ZrAlO	2-BuOH	150	_	8	99.0	96.8	58
6	Cu/ZnO/Al ₂ O ₃	Isopropanol	120	_	3	96.0	86.4	59
7	RANEY®	Isopropanol	r.t.	0.1 Ar	9	_	99.0	60
8	MoS ₂ /AC	Isopropanol	230	1	1.5	97.2	88.7	This work

^a External H₂.



Fig. 6 The recycling test of 8 wt% MoS_/AC. Reaction conditions: EL 2 mmol, catalyst 75 mg, isopropanol 20 mL, 230 °C, 1.5 h, 1 MPa H_2.

Our XPS characterization (Fig. S8†) showed that the percentages of Mo^{4+} and S^{2-} decreased gradually with each cycle, and more MoO_3 was generated, which is in accordance with the literature and our recycling results. It's worth noting that this may not be solely responsible for the decline in catalyst activity after consecutive cycles, because metal sintering and leaching also had an important impact. The intensity of the Mo XPS signal also decreased after different uses, as shown in Table S2,† based on the XPS quantitative analysis. Both Mo and S contents presented apparent loss after the reaction because of metal leaching during the reaction. Fortunately, the sulfide state of the catalyst can be easily regenerated by sulfidation before using for the next cycle. Therefore, we re-sulfurized the 4th MoS_2/AC and the conversion of EL and selectivity of GVL could reach 86.4% and 88.3%, respectively.

4. Conclusion

In this work, a series of MoS_2 -based supported catalysts were prepared by the impregnation method and employed

in the CTH of EL to GVL. The 8 wt% MoS₂/AC catalyst was found to exhibit the highest catalytic performance in the CTH reaction under 1 MPa H₂ at 230 °C for 1.5 h in isopropanol solvent, with the EL conversion of 97.2% and GVL yield of 88.7%. By comprehensive characterization and catalytic measurements, we found that the CTH activity of EL to GVL is closely related to the MoS₂ morphology and acid distribution on the support. Among the catalysts with different supports, the AC support with abundant Lewis acid sites and large surface area facilitated the high dispersion of lower stacked MoS₂, and the MoS₂-acid synergistic catalysis contributed to the superior activity and selectivity. We further investigated the effect of reaction conditions, different H-donors, and substrates during the CTH reaction, and proposed a plausible reaction pathway and mechanism over MoS₂/AC. Although this MoS₂/AC catalyst presented comparable GVL yield with those reported in the literature, the harsh reaction conditions and the obvious deactivation are non-negligible which will limit its further application. More studies are needed to focus on the enhancement of low-temperature activity and stability in the future.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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