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Quantitative production of butenes from biomass-derived γ -valerolactone catalysed by hetero-atomic MFI zeolite

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Efficient production of light olefins from renewable biomass is a vital and challenging target to achieve future sustainable chemical processes. Here we report a hetero-atomic MFI-type zeolite (NbAIS-1), over which aqueous solutions of γ -valerolactone (GVL), obtained from biomass-derived carbohydrates, can be quantitatively converted to butenes with a yield of >99% at ambient pressure under continuous flow conditions. NbAIS-1 incorporates simultaneously niobium(V) and aluminium(III) centres into the framework and thus has a desirable distribution of Lewis and Brønsted acid sites with optimal strength. Synchrotron X-ray diffraction and absorption spectroscopy show that there is cooperativity between Nb(V) and Brønsted acid sites on confined adsorption of GVL, while the catalytic mechanism for conversion of confined GVL to butenes is revealed by *in situ* inelastic neutron scattering, coupled with modelling. This study offers a prospect for the sustainable production of butene as a platform chemical for the manufacture of renewable materials.

Approximately 400 million tonnes of light olefins (ethene, propene and butenes) are produced each year for polymer, chemical and pharmaceutical industries¹⁻⁶. State-of-the-art processes are based on stream cracking of naphtha and thus critically rely on fossil fuels, possessing significant environmental impacts¹. Catalytic production of light olefins from renewable plant biomass is a highly promising target⁷, and many processes have been developed to bridge future gaps in the supply of commodity chemicals from biomass⁸⁻¹¹. In particular, biomass-derived γ -valerolactone (GVL), obtained from agricultural waste *via* low-cost, high-yield commercial processes (production scale at 27 tonnes in 2018), has been identified as a sustainable resource to produce butenes¹², which, through well-established petroleum processes, can be readily transformed to a wide spectrum of petrochemicals, such as propene^{2,13}, 1,3-butadiene¹⁴, aromatics¹⁵, liquid fuels^{2,9}, polyethylene^{2,16} and polybutene^{2,17}. In this respect, development of efficient catalytic processes to convert GVL to butenes is of vital importance. This conversion involves the ring-opening and decarboxylation reactions catalysed over solid acids, and amorphous $\text{SiO}_2/\text{Al}_2\text{O}_3$, ZSM-5, La/ZSM-5, $\text{Ni}_2\text{P}/\text{MCM-41}$, Zn-AlPO-5 and $\text{Pd}/\text{Nb}_2\text{O}_5$ have been studied^{9,15,18-24}. Using a 30 wt% GVL feedstock at 375 °C and atmospheric pressure, a butene yield of 75% has been achieved over the $\text{SiO}_2/\text{Al}_2\text{O}_3$ catalyst⁹. Commercial supplies of GVL from biorefineries are aqueous solutions with GVL concentrations between 20-40 wt%¹⁵; however, the water in the reaction can partially or completely deactivate solid-acid catalysts by coordinating to the acid sites and forming acid-base adducts^{25,26}. Thus, the design of an efficient, yet water-tolerant catalyst for this

conversion remains a fundamental challenge. Recently, emerging niobium-based catalysts have shown to possess marked water-tolerance^{25–32} and exceptional activities for the hydrodeoxygenation of biomass under mild conditions^{33–35}.

Here, we describe the development of a hetero-atomic MFI-type zeolite (denoted as NbAIS-1) and its catalytic activity for the conversion of GVL to butenes. NbAIS-1 integrates, for the first time, both Nb(V) and Al(III) sites into the framework, and through fine-tuning of the ratio of Nb:Al:Si, optimal acidity and hence reactivity of the catalyst can be achieved, promoting a quantitative production of butenes (yield >99%) using a 30 wt% GVL feedstock at 320 °C and atmospheric pressure in absence of an external source of hydrogen. NbAIS-1 shows superior water-tolerance and catalytic stability over 180 hours in a continuous-flow reaction. The underlying catalytic mechanism has been elucidated at a molecular level, employing a combination of *in situ* synchrotron X-ray powder diffraction (SXPd), X-ray absorption spectroscopy (XAS), inelastic neutron scattering (INS) and DFT calculations. These complimentary techniques revealed that the cooperativity between Nb(V) and Brønsted acid sites plays a key role in the reactivity of GVL and, compared with conventional HZSM-5, the absence of strong Brønsted acid sites in NbAIS-1 effectively hindered the formation of by-products, resulting in the observed selectivity of butenes.

Synthesis and characterisation. The hydrothermal synthesis of ZSM-5 doped with varying loadings of Nb(V) (0-5.58wt%) and Al(III) (0-1.64 wt%) has been systematically studied, and all obtained materials exhibit the MFI-type framework (Supplementary Fig. 1), BET surface areas of 357-408 m²g⁻¹ (Supplementary Table 1), and particle size distributions between 300-500 nm (Supplementary Fig. 2, Supplementary Table 1). All zeolites studied here exhibit similar micropore volumes (Supplementary Table 1). An optimal loading of 3.81wt% Nb(V) and 1.64wt% Al(III) has been identified for the synthesis of NbAIS-1(0.027/0.04/1) (yield=95%). The atomic ratio of Nb/Al/Si has been determined by energy dispersive X-ray (EDX) analysis to be 0.027/0.04/1 with homogeneous distributions of metal ions (Fig. 1a-e). The vibrational modes of Nb-O-Si moieties³⁶ in NbAIS-1(0.027/0.04/1) have been observed by FTIR (971 cm⁻¹; Fig. 1f) and Raman spectroscopy (921 and 973 cm⁻¹; Fig. 1g), indicating the incorporation of Nb(V) centres as the framework T-sites.

The successful incorporation of Nb(V) and Al(III) into framework sites is further confirmed by electron paramagnetic resonance (EPR) spectroscopy. Although NbS-1 (the isostructural analogue with 0%

Al loading) and NbAIS-1 are EPR silent due to the diamagnetic Nb(V) and Al(III) ions, characteristic paramagnetic centres can be induced by γ -irradiation of the zeolites³⁶. EPR spectra of γ -irradiated NbS-1(0.027/1) and NbAIS-1(0.027/0.04/1) show a wide, structured signal that spreads over a magnetic field range of *ca.* 350 mT (Fig. 1h) with a 10-line hyperfine structure, consistent with coupling of an unpaired electron to a ⁹³Nb nucleus ($I = 9/2$; 100% natural abundance). The site has axial symmetry with $g_{\parallel} = 1.866$, $g_{\perp} = 1.935$ and hyperfine couplings of $A^{\text{Nb}}_{\parallel} = 0.0289$, $A^{\text{Nb}}_{\perp} = 0.0148 \text{ cm}^{-1}$ (Supplementary Table 2), consistent with the previous characterisation of Nb(IV) centres generated at the *pseudo*-tetrahedral NbO₄ units in the framework of silicalite-1³⁶, whereas this signal is not observed in γ -irradiated HZSM-5 or Nb₂O₅-HZSM-5 mixtures (Fig. 1h), indicative that the Nb(V) ion in NbAIS-1 is solely incorporated into framework sites, rather than deposited as Nb₂O₅ phases. A second narrow signal with hyperfine structure observed in the spectra of γ -irradiated HZSM-5 and NbAIS-1 (Fig. 1i, Supplementary Table 2), arises from an electron hole defect on a framework oxygen atom in an Al-O[•]-Si site³⁷, where the structure arises from hyperfine coupling with the ²⁷Al nucleus ($I = 5/2$; 100% natural abundance). In γ -irradiated NbS-1, a sharp signal is observed, but the hyperfine structure is lost, consistent with the absence of Al(III). Thus EPR measurements provide convincing evidence for the incorporation of both Nb(V) and Al(III) into framework sites in NbAIS-1, enabling the fine-tuning of its framework acidity and hence catalytic activity.

Pyridine-adsorption FTIR (Py-IR) spectroscopy has been used to characterise the nature of acidity in these zeolites (Supplementary Fig. 3 and Supplementary Table 3). NbS-1 exhibits solely Lewis acidity due to the presence of Nb(V), whereas NbAIS-1 shows both Lewis and Brønsted acidity, which arises from the dual functionality of Nb(V) and Al(III) sites. Notably, the nature of the acidity in NbAIS-1 is distinct to that of HZSM-5: the ratio of Lewis/Brønsted acid sites in NbAIS-1 is 4.69, twelve times that of HZMS-5. The acidity has been quantified by ammonia temperature-programmed desorption (NH₃-TPD) (Supplementary Fig. 4 and Supplementary Table 3). HZSM-5 displays both strong and weak acid sites with a total amount of 0.4-0.63 mmol g⁻¹ and NbS-1 exhibits minor weak acid sites of 0.04 mmol g⁻¹. Interestingly, NbAIS-1 shows only weak acid sites, but their concentration is considerably higher (0.22 mmol g⁻¹) than that of NbS-1. Thus, doping of pentavalent niobium sites into the zeolite can effectively tune the nature and distribution of framework acidity and provides an excellent platform to examine the resultant catalytic activities.

Catalytic tests. Conversions of pure GVL have been firstly performed over a fixed-bed packed with the catalysts under flow conditions at 320 °C (WHSV = 0.18 h⁻¹; Table 1). HZSM-5 with varying Al/Si ratios show GVL conversions of 75-92% and moderate butene yields of 33.1-44.1% (Entries 1-3). This is due to the formation of considerable amounts of 2-cyclopentenone, aromatics, polycyclic aromatics as by-products and coke over strong acid sites (Supplementary Figs. 5 and 6). On the other hand, the lack of Brønsted acid sites in NbS-1 gives very low butene yields (~7%) and GVL conversions (32%) (Entries 4 and 5). In contrast, a 96% GVL conversion with 80.4% butene yield has been achieved over NbAIS-1(0.027/0.04/1) (Entry 6). This suggests that the strength and nature of the framework acidity are key parameters for optimising its performance. By introducing Nb(V) as weak Lewis acid sites to weaken the strong Al(III) acid sites in NbAIS-1, the formation of by-products was effectively inhibited, leading to high selectivities to butenes over NbAIS-1.

The catalytic performance of these zeolites has been further tested using 30wt% and 60wt% aqueous solution of GVL (Table 1 and Supplementary Table 4); the former is of direct relevance to practical processes¹⁵. The butene yields from aqueous solutions of GVL over HZSM-5 with varying Si/Al ratio decreased to 22.2-29.2% owing to the deactivation of acid sites in the presence of water (Entries 1-3, 11 and 13-15). Significantly, quantitative production of butenes (yield >99%) has been achieved over NbAIS-1(0.027/0.04/1) using a 30wt% GVL feedstock (Entry 16), demonstrating the significantly improved water tolerance by Nb(V) doping. Other widely-studied Nb-containing catalysts, such as Nb₂O₅, niobic acid (Nb₂O₅·H₂O) and NbOPO₄, have also been tested for this reaction and, as expected, these catalysts all exhibit excellent water tolerance (Entries 8-10 and 17-19). A butene yield of 78.3% has been obtained from the conversion of 30wt% aqueous solutions of GVL over NbOPO₄, which however has a much lower utilisation efficiency of Nb compared with NbAIS-1(0.027/0.04/1) (46% and 3.8%, respectively, in terms of Nb concentration). The performance of NbAIS-1(0.027/0.04/1) compares favourably with all state-of-the-art catalysts (Supplementary Table 5). As previously observed in niobic acids systems, water can only partially coordinate to Nb(V) centres, leaving sufficient positive charges on NbO₄ moieties to bind substrates^{26,31}. Indeed, the formation of coke, 2-cyclopentenone and other by-products is effectively inhibited over NbAIS-1(0.027/0.04/1) by the presence of water (Supplementary Fig. 7 and Table 1). The excellent stability of NbAIS-1(0.027/0.04/1) has been demonstrated by both cycling and time-on-stream tests, where the yield of butenes remained at >99% after 180 hours of reaction (Fig. 2a-b). The used catalyst has been characterised

by N₂-sorption, synchrotron XPD, EDX, FTIR, EPR (upon ⁶⁰Co γ -irradiation), XAS, ²⁷Al NMR, NH₃-TPD and pyridine-IR (Fig. 2c-d, Supplementary Figs. 8-12). Importantly, all these results confirm that there is little change on the structure and acidic sites of used NbAIS-1, demonstrating the excellent structural stability of the bifunctional zeolite. Interestingly, little change was observed on the structure and acidic sites of used HZSM-5(0.04/1) (Fig. 2c-d, Supplementary Figs. 11-13), indicating that the decrease of catalytic activity of HZSM-5 upon exposure to water compared with reactions using pure GVL (Table 1, entries 2, 11 and 14) is primarily due to partial poisoning of acidic sites, consistent with the literature reports^{25,26}.

Studies of the coordination environment of Nb(V) sites. To understand the effect of active Nb(V) sites, their local environment was interrogated through Nb K-edge XAS. The absorption edge positions for both NbAIS-1(0.027/0.04/1) and NbS-1(0.027/1) from X-ray absorption near edge spectra (XANES) are consistent with the pentavalent oxidation state³⁸ with the as-prepared samples exhibiting a common weak pre-edge peak (Fig. 3a). The weak nature of this pre-edge feature can be attributed to disruption of the *pseudo*-tetrahedral Nb environment *via* water coordination (Fig. 3b)³⁸. On adsorption of GVL to the pores of NbAIS-1, the pre-edge position is further influenced with an apparent blue-shift (~0.8 eV); in contrast, no shift is witnessed for NbS-1. This reflects both greater electron donation from GVL³⁹, but also the preferred adsorption geometry within the bifunctional zeolite NbAIS-1, which facilitates closer interaction between the Nb(V) sites and the substrate. This conclusion is verified through extended X-ray absorption fine structure (EXAFS) analysis (Fig. 3c). Fitting of the first coordination shell reveals an increase in the average Nb=O bond length due to the presence of an adsorbate and subsequent decrease in double bond nature, whilst the siloxane bridges remain unaffected (Supplementary Table 6). The effect is apparent in both NbAIS-1 and NbS-1 systems, and the NbAIS-1 system is perturbed to a significantly greater extent, 0.22 *vs* 0.06 Å increase in bond length, respectively. Furthermore, fitting of the second coordination shell discredits the potential for bulk Nb₂O₅ formation, which confirms the location of Nb(V) to be solely within the framework, consistent with the EPR observation. Thus, the framework Nb(V) site plays a key role in the adsorption of GVL in NbAIS-1.

Determination of adsorption domains for GVL. The binding domains of GVL within these zeolites have been determined from *in situ* SXPD data (Supplementary Fig. 14 and Supplementary Note

Interaction between GVL and Nb/Al/H sites). All datasets enabled direct observation of two independent binding sites for GVL (I and II) within the pores (typical $R_{wp} = 4\text{-}6\%$; Fig. 4, Supplementary Fig. 15, Supplementary Tables 7-12) without notable structural phase change of the framework (Supplementary Fig. 14). GVL^I and GVL^{II} are located near the intersection of straight and sinusoidal channels, respectively (Fig. 4a-c). Importantly, adsorbed GVL molecules show three distinct spatial orientations within the framework of HZSM-5, NbS-1 and NbAIS-1, indicating the presence of varying host-guest interactions. In the straight channel of HZSM-5, GVL^I interacts with a bridging O(H)-centre through its C=O group [$C=\underline{O}\cdots\underline{O} = 3.812(54) \text{ \AA}$] *via* a weak hydrogen bond (Fig. 4d). In NbS-1, GVL^I directly binds to framework T-sites (NbO₄ moieties) *via* its intra-ring O-centre [$T\cdots\underline{O}C_4 = 4.005(39) \text{ \AA}$] (Fig. 4e). Interestingly, adsorbed GVL^I in NbAIS-1 forms host-guest interactions with both bridging O(H)-centres and T sites [$C=\underline{O}\cdots\underline{O} = 3.574(141) \text{ \AA}$; $Nb\cdots\underline{O}C_4 = 3.789(75) \text{ \AA}$] (Fig. 4f). Similar but more notable observations are observed for GVL^{II} (Fig. 4g-i). For example, GVL^{II} forms a weak hydrogen bond interaction to a bridging O(H)-centre [$C=\underline{O}\cdots\underline{O} = 3.210(38) \text{ \AA}$] in HZSM-5 and a dipole interaction to the framework T-site [$Nb\cdots\underline{O}C_4 = 3.560(40) \text{ \AA}$] in NbS-1, whereas in NbAIS-1, it displays a combination of these two types of interactions [$C=\underline{O}\cdots\underline{O} = 3.055(57) \text{ \AA}$; $Nb\cdots\underline{O}C_4 = 3.490(75) \text{ \AA}$]. These results strongly indicate that Brønsted or Lewis acid sites alone in HZSM-5 or NbS-1 can only serve as “mono-dentate” binding sites for GVL molecules, whereas the cooperativity between these two types of acid sites results in the optimal adsorption of GVL *via* a “chelating” mechanism in NbAIS-1. Recently, the distribution of SiO(H)Al sites in LTA zeolite has been studied using periodic DFT calculations and INS^{40,41}. Here, ²⁹Si NMR, INS and DFT calculations demonstrate the presence of NbO(SiO)_nAl (n=1 or 2) species in NbAIS-1, which promotes the preferred adsorption of GVL in NbAIS-1 (Supplementary Figs. 16-18, Supplementary Tables 13-15, and Supplementary Note Distribution of Nb/Al/H sites). Thus, the excellent catalytic activity of NbAIS-1 for butene production is originated from (i) the highly confined adsorption of GVL in the framework pores; (ii) greatly reduced Brønsted acidity of the resultant framework (~70% comparing to HZSM-5), leading to the rapid desorption of butene products from the catalyst surface, thus preventing their further reactions to form various cyclic by-products and cokes.

Studies of reaction mechanism. Combined INS and DFT calculations have been applied to investigate the vibrational dynamics of GVL@NbAIS-1(0.027/0.04/1) *in operando*. Recently, this technique has been employed to investigate the vibrational dynamics of C₃H₆@ZSM-5.⁴² The INS spectra of solid and

adsorbed GVL were recorded and modelled *via* DFT calculations (Supplementary Figs. 19-23, Fig 5a-b, Supplementary Table 16 and Supplementary Note inelastic neutron scattering), allowing a full assignment of the spectral features for GVL. Comparison of INS spectra of adsorbed GVL (spectrum of empty cell has been subtracted) and solid GVL shows a number of observations (Fig. 5a). There is little change in the low-energy modes ($<100\text{ cm}^{-1}$) of GVL on adsorption, indicating adsorbed GVL molecules are highly ordered and confined within the framework. The peaks at 1060 cm^{-1} (assigned to C4-O1 stretching) and at 1127 cm^{-1} (assigned to C1-O1-C4 asymmetric stretching) decrease significantly in intensity and shift to 1046 cm^{-1} and 1121 cm^{-1} , respectively, indicating that C4-O1 and C1-O1 bonds are activated on adsorption *via* O1 to the Nb(V) site. Meanwhile, the peaks at 151 cm^{-1} (assigned to C4 out-of-plane wagging) and at 827 cm^{-1} (assigned to ring distortion) also decrease in intensity owing to the hindered motion of O1 on adsorption. The modes of C4-C5 torsion (273 cm^{-1}) and rocking (317 cm^{-1}) are also affected by adsorption *via* the O1 centre, and shift to lower energy at 234 and 308 cm^{-1} , respectively. The marked red-shift of $\Delta = 39\text{ cm}^{-1}$ for the torsion mode confirms the restricted motion of the methyl group on adsorption [$-\text{CH}_3\cdots\text{O}_{\text{zeolite}} = 2.032(65)\text{ \AA}$]. The rocking mode of C1=O2 (512 cm^{-1}) has disappeared completely, consistent with the formation of hydrogen bonds to the Brønsted acid site. The peak at 181 cm^{-1} (assigned to the twisting mode of O2=C1-C2) shifts to 173 cm^{-1} , further confirming the adsorption of GVL *via* the O2 centre on the Brønsted acid sites. These findings are highly consistent with the X-ray crystal structures.

Adsorbed GVL molecules on NbAIS-1(0.027/0.04/1) underwent a first catalytic conversion at $280\text{ }^{\circ}\text{C}$ for 3 minutes (Fig. 5a). The peaks at 1046 , 1121 and 827 cm^{-1} (all involving C4-O1 vibrational modes) further reduce in intensity, indicating that the C4-O1 bond has been selectively activated. To promote further conversion, a second reaction was carried out at $300\text{ }^{\circ}\text{C}$ for 3 minutes (Fig. 5a). All INS features related to C4-O1 modes (1046 and 1121 cm^{-1}) and ring deformation (609 , 655 , 802 , 827 and 899 cm^{-1}) have disappeared, suggesting the ring-opening reaction *via* selective cleavage of the C4-O1 bond in activated GVL. Meanwhile, O2 is protonated, leading to the decrease of peak intensities at 530 and 173 cm^{-1} (assigned to C1 and C2 out-of-plane wagging modes, respectively). A final reaction was conducted at $320\text{ }^{\circ}\text{C}$, and these two peaks (530 and 173 cm^{-1}) disappeared, consistent with the decarboxylation reaction *via* cleavage of the C1-C2 bond (Fig. 5a). Meanwhile, new features appeared at 212 , 229 , 254 , 366 , 407 and 437 cm^{-1} , fully consistent with the formation of butenes (Supplementary Fig. 24).

A full catalytic circle has been constructed based upon the structural, dynamic and modelling results (Fig. 5c). Over NbAIS-1, the adsorption of GVL occurs on Nb(V) and Brønsted acid sites in a “chelating mode” *via* O1 and O2 centres, followed by a ring-opening reaction of activated GVL *via* selective cleavage of the C4-O1 bond at elevated temperatures. Meanwhile, C1=O2 is protonated *via* proton transfer from the Brønsted acid sites. On addition of the H-shift in C₅-skeleton, a β -scission occurs and C1-C2 bond is cleaved, yielding butenes and an equimolar CO₂. By contrast, on HZSM-5, both the ring-opening and decarboxylation reactions proceed on the Brønsted acid sites (Fig. 5d). The inability for the intermediate carbocation to desorb from the strong acid sites of HZSM-5 results in its transformation to undesirable by-products of 2-cyclopentenone, aromatics and coke *via* dehydration, aromatisation and coking, respectively.

Outlook

Powerful drivers exist for the development of efficient catalysts to enable the sustainable production of light olefins from biomass to remit our reliance on fossil fuels. NbAIS-1, integrating both Nb(V) and Al(III) sites into the MFI-zeolite framework, demonstrates an excellent catalytic performance to transform biomass-derived GVL in aqueous solutions to butenes with a quantitative yield. Nb(V) sites in the MFI framework play three vital roles: i) optimising acidity of zeolite to hinder the production of by-products; ii) cooperating with Brønsted acid sites for confined adsorption of GVL and thus activating C-O bonds; iii) resisting to water poisoning and thus enhancing the overall catalytic stability. Upon reaction completion, the liquid phase product contains only water and gas phase product is an equimolar mixture of butenes and CO₂, which can be facilely separated based upon the difference in their boiling points ($\Delta=72$ °C). While butenes are used as a platform chemical, recovered CO₂ can be readily sequestered. The industrial-scale synthesis of NbAIS-1 could be achieved based upon the infrastructure widely used for the synthesis of ZSM-5, which coupled with its high stability, further demonstrates its potential for practical applications.

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Author contributions: L.L. and M.F carried out syntheses and characterisation of the zeolite samples. L.L. and X.H. carried out catalytic tests. L.L., A.M.S, F.T. and E.J.L.M collected and analysed EPR data. L.L. and C.M.A.P. collected and analysed the XAS data. L.L., J.C., I.D.S. and C.C.T. collected and analysed the synchrotron X-ray diffraction data. Z.T and Y.L. collected and analysed the py-IR data. L.L., Y.C, L.L.D., S.R. and A.J.R. collected and analysed the neutron scattering data and carried out DFT modelling. S.Y. was responsible for the overall direction of the project and preparation of the manuscript, with contributions from all authors.

Methods

Catalyst preparation. HZSM-5 samples were purchased from Alfa Aesar and denoted as HZSM-5(Al/Si mole ratio). NbAIS-1 and NbS-1 samples were prepared by hydrothermal synthesis, and denoted as NbAIS-1(Nb/Al/Si mole ratio) and NbS-1(Nb/Si mole ratio), respectively. In a typical synthesis, aluminium isopropoxide (99.99+%, Sigma Aldrich) was first dissolved in deionised water, into which tetrapropylammonium hydroxide solution (TPAOH, 1.0 M in H_2O , Sigma Aldrich) as the structure-directing agent was added. After the mixture was stirred at room temperature for 2h, niobium ethoxide (99.95%, Sigma Aldrich) was added and the mixture was stirred for another 2h. Then tetraethyl orthosilicate (98%, Sigma Aldrich) was added dropwise and the mixture was stirred for another 2h, resulting in a gel with a chemical composition of $1\text{Si} : x\text{Al} : y\text{Nb} : 0.25\text{TPAOH} : 15\text{H}_2\text{O}$ (x and y were determined by the target Al/Si and Nb/Si mole ratios, respectively). The gel was transferred into a 46-mL Teflon-lined stainless steel autoclave, which was sealed and heated at 170 °C for 48h. The solid products were centrifuged, washed with deionised water, dried overnight at 80°C, and finally calcined at 550°C under air flow for 6h. NbS-1 samples were synthesised by the same procedure but without the addition of aluminium isopropoxide. Except the yield (30%) of NbAIS-1(0.04/0.027/1), the typical yields of all zeolites in this study are 90-95%. NbOPO_4 was synthesised by a hydrothermal method at pH = 2 according to literature⁴³. Nb-oxide (Nb_2O_5) and niobic-acid ($\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$) samples were purchased from Sigma Aldrich and CBMM, Brazil, respectively. The methods of zeolite characterisation were described in detail in Supplementary Methods Catalyst characterisation.

Catalytic testing. Catalytic reactions were carried out in a stainless steel continuous-flow reactor (12.7 mm i.d.). Two grams of catalyst was pressed, crushed, and sorted into grains by 40–60 meshes, which were then activated at 450 °C for 3h under a nitrogen flow before the reaction. GVL was injected into nitrogen flow (50 mL min^{-1}) by syringe pump (Cole-Parmer) and passed through the reactor at the target temperature. The output liquid products were collected and analysed by Agilent 7890B gas chromatography equipped with a HP-5 column ($30 \text{ m} \times 0.32 \text{ mm} \times 0.25 \text{ }\mu\text{m}$) and Agilent 6890N–Agilent 5973N gas chromatography–mass spectrometry (GC–MS) equipped with HP-5MS column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ }\mu\text{m}$). The output gas products were collected and analysed by Agilent Micro GC 490 equipped with PoraPLOT U column (length 10 m) and Agilent 7890A–Agilent 5975C GC-MS equipped with HP-PLOT/Q

column (30 m × 0.53 mm × 40 μm). GVL conversion is calculated by equation i.e. $\text{GVL conversion} = (\text{GVL}_{\text{in}} - \text{GVL}_{\text{out}}) / \text{GVL}_{\text{in}} \times 100\%$, where GVL_{in} and GVL_{out} denote the moles of GVL in the feed and exit, respectively. Product selectivity is calculated in carbon basis, i.e. $S_i = (a_i \times n_i) / (\sum a_i \times n_i) \times 100\%$, where a_i and n_i denote the carbon number and mole of product i , respectively. CO_2 is excluded in selectivity calculation. Product yield is calculated by $\text{Yield} = \text{Conversion} \times \text{Selectivity} \times 100\%$. Total carbon balances for the production from GVL typically closed to within 5%.

X-ray absorption spectroscopy. Transmission Nb K-edge X-ray absorption spectra were collected on beamline B18 at Diamond Light Source, employing a water-cooled Si [3 1 1] double crystal monochromator and double toroidal Pt-coated mirror for beam focusing. Data collection spanned 200 eV before the edge to 1000 eV above it, step size of 0.5 eV; with reference, Nb foil spectra simultaneously collected to enable energy calibrations. GVL saturated samples were collected as a slurry, contained within a sealed Kapton capillary. Data processing was carried out in the Demeter open source software package, version 0.9.26, with XAS spectra processing (normalisation and background subtractions) and EXAFS fitting conducted within the Athena and Artemis programs within Demeter respectively. Reference niobium oxide standards, NbO_2 and Nb_2O_5 , were also collected after dilution in boron nitride.

High-resolution synchrotron X-ray powder diffraction (SXPd) and Rietveld refinement. SXPd data were collected on Beamline I11, Diamond Light Source, UK [wavelength=0.824869(10) Å] at room temperature. The zeolite powder was loaded in a 0.7 mm borosilicate glass capillary. High-resolution diffraction data were obtained from the samples using the multi-analyser crystal (MAC) detectors. The patterns were collected in the 2θ range 0-150° with 0.001° data step. Using the TOPAS software, the SXPd patterns were refined by the Rietveld methods. The Thompson-Cox-Hastings pseudo-Voigt peak function⁴⁴ was applied to describe the diffraction peaks. The scale factor and lattice parameters were allowed to refine for all diffraction patterns. The refined structural parameters include the fractional coordinates (x, y, z) and isotropic displacement factors (Beq) for all atoms, and the site occupancy factors (SOF) for all Nb, Al, Si species and GVL molecules. The quality of the Rietveld refinements has been assured with low goodness-of-fit (gof) factors, low weighted profile factors (Rwp) and well-fitted patterns with reasonable isotropic displacement factors (Beq) within experimental errors.

Inelastic neutron scattering. INS spectra were recorded on the VISION spectrometer at Spallation Neutron Source, Oak Ridge National Laboratory (USA), as well as the TOSCA spectrometer at the ISIS Facility at the STFC Rutherford Appleton Laboratory (UK). Both VISION and TOSCA are indirect geometry crystal analyser instruments that provide a wide dynamic range with high resolution. All the INS spectra were collected after the sample was cooled and stabilised at temperatures below 15 K.

The adsorption/reaction experiments were conducted at beamlines TOSCA and VISION and results obtained from both spectrometers are consistent. In a typical experiment, the catalyst (~11 g) was loaded into a flow-type stainless steel cell that can also be used as a static cell with all valves closed. The sample was heated at 450 °C (5 °C/min ramping) under He for 3 h to remove any remaining trace water before the experiment. Then 20 mmol GVL was injected into the cell at 135 °C. Before the data collection, the cell was flushed using dry He to remove weakly bound GVL molecules. The samples were cooled to <15 K during data collection. After each reaction, the cell was flushed with dry He, sealed and cooled for INS collection to detect the presence of possible reaction intermediates. INS spectra of pure solid compounds for both starting material and reaction products were collected at 5 K. The methods of DFT calculations and modelling of the INS spectra were shown in Supplementary Methods DFT calculations and modelling of the INS spectra.

Data availability. All relevant data are available from the authors, and/or are included with the manuscript.

Method References:

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Author Information: The crystal structures are available free of charge from the Cambridge Crystallographic Data Centre under reference number CCDC-1888752-1888753 and CCDC-1889968-1889969. Reprints and permissions information is available at www.nature.com/reprints. The authors declare no competing financial interests. Correspondence and requests for materials should be addressed to S.Y. (Sihai.Yang@manchester.ac.uk).

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Figures and Tables:

Fig. 1. Physical characterisation of catalysts. (a) EDX spectra of HZSM-5(0.04/1), NbS-1(0.027/1) and NbAIS-1(0.027/0.04/1), (b) SEM image of NbAIS-1(0.027/0.04/1), EDX map of Si K_α (c), Al K_α (d) and Nb L_α (e) in NbAIS-1(0.027/0.04/1). The peaks in regions of 0.52, 1.49, 1.74 and 2.17 keV are related to the binding energies of O K_α, Al K_α, Si K_α and Nb L_α, respectively. (f) FTIR and (g) Raman spectra of HZSM-5(0.04/1), NbS-1(0.027/1) and NbAIS-1(0.027/0.04/1) samples. X-band (*ca.* 9 GHz) EPR spectra of activated zeolites by γ -irradiation at 77 K: (h) wide magnetic field-sweep, highlighting the induced Nb(IV) signals in NbS-1(0.027/1) and NbAIS-1(0.027/0.04/1) and; (i) narrow magnetic field-sweep, highlighting the induced electron hole defect Al-O[•]-Si signals in NbAIS-1(0.027/0.04/1) and HZSM-5(0.04/1). The weak features at *ca.* 304 and 356 mT in (i) are due to radiation induced trapped H atoms. Experimental spectra are shown in black, red, blue and magenta. Simulated spectra of Nb(IV) (h) and Al-O[•]-Si defects (i) are shown in grey.

Fig. 2. Catalysts stability. (a) Comparison of butene yield over 15 cycles of reactions over NbAIS-1(0.027/0.04/1) at 320 °C using bulk GVL (99%) as the feed. After each cycle, the catalyst is calcined at 550 °C under an air flow. (b) Lifetime study of NbAIS-1(0.027/0.04/1) and HZSM-5(0.04/1) at 320 °C using 30wt% GVL in aqueous solution as the feed. The yield of butene remained at >99% after 180 hours of continuous reaction. Comparison of (c) SXPD patterns [$\lambda = 0.82487(1) \text{ \AA}$] and (d) acidities determined by pyridine-IR of HZSM-5(0.04/1) and NbAIS-1(0.027/0.04/1) before and after the conversion of 30wt% GVL at 320 °C for 180h.

Fig. 3. Nb K-edge X-ray absorption spectroscopy (XAS) for Nb-containing zeolites. (a) XANES spectra highlighting both edge position and pre-edge feature of the Nb-containing samples. (b) Shifts of pre-edge feature in NbAIS-1, with inset showing the 1st derivate in the presence of water and GVL substrates. (c) Phase-corrected, k₃-weighted Fourier transform of the EXAFS spectra and fitting curves (dot line) for NbAIS-1 as-prepared and saturated in GVL.

Fig. 4. Views of crystal structures of GVL-loaded HZSM-5(0.04/1), NbS-1(0.027/1) and NbAIS-1(0.027/0.04/1). All models were obtained from Rietveld refinements based upon *in situ* synchrotron X-ray powder diffraction data. Two distinct binding sites for GVL have been observed in the straight channel (I) and the sinusoidal channel (II). (a) HZSM-5(0.04/1)·8GVL ($\text{Al}_{3.692}\text{Si}_{92.308}\text{O}_{192}\cdot 8\text{C}_5\text{H}_8\text{O}_2$), (b) NbS-1(0.027/1)·8GVL ($\text{Nb}_{2.524}\text{Si}_{93.476}\text{O}_{192}\cdot 8\text{C}_5\text{H}_8\text{O}_2$), (c) NbAIS-1(0.027/0.04/1)·8GVL ($\text{Al}_{3.599}\text{Nb}_{2.429}\text{Si}_{89.972}\text{O}_{192}\cdot 8\text{C}_5\text{H}_8\text{O}_2$). The details of the host-guest binding are enlarged in d-i. Detailed views of GVL^I (d,e,f) and GVL^{II} (g,h,i) in HZSM-5(0.04/1), NbS-1(0.027/1) and NbAIS-1(0.027/0.04/1), respectively. GVL molecules and the functional sites involved in the cooperative binding are highlighted by the use of an amplified ball-and-stick model (Nb/Al/Si, green; C, grey; O, red; H, white). The O1...Nb interactions, O2...O(H) interactions are highlighted in cyan and blue, respectively. Owing to the uncertainty on locations of protons, all hydrogen bonds in this report are described as the distance between the O_{GVL} and the O_{zeolite} centres.

Fig. 5. Inelastic neutron scattering (INS) spectra for NbAIS-1(0.027/0.04/1) on the adsorption and catalytic conversion of GVL and proposed reaction mechanisms. All spectra shown here are after the subtraction of INS spectrum of the empty cell. No abscissa scale factor was used throughout this report for INS calculations. Where no error bars are visible these are smaller than the symbols used to represent the data points. **(a)** Comparison of INS spectra for condensed solid GVL, adsorbed GVL, and reacted GVL on NbAIS-1(0.027/0.04/1). **(b)** Selected vibrational modes of GVL. The wavenumbers of adsorbed GVL as observed by experiments are shown in parentheses. For clarification, H atom (white) is only displayed in the first GVL model. Proposed reaction mechanisms for the conversion of GVL over **(c)** NbAIS-1 based on INS/SXPD experiments and **(d)** HZSM-5 based on literature reports^{13,18,21}.

Table 1. Summary of the GVL conversion and product yields over different catalysts^a.

Entry	Catalyst	GVL concentration (wt %)	GVL conversion (%)	Yield (mol %)			
				Butene	2-cyclopentenone	Aromatics	Others ^b
1	HZSM-5(0.027/1)	99	75	33.1	9.9	10.3	21.7
2	HZSM-5(0.04/1)	99	83	37.9	11.5	12.4	21.2
3	HZSM-5(0.067/1)	99	92	44.1	13.4	12.9	21.6
4	NbS-1(0.027/1)	99	31	6.9	0.4	0	23.7
5	NbS-1(0.04/1)	99	32	7.2	0.4	0	24.4
6	NbAlS-1(0.027/0.04/1)	99	96	80.4	6.2	0.2	9.2
7	NbAlS-1(0.04/0.027/1)	99	84	56.3	4	0.2	23.5
8	Nb ₂ O ₅	99	8	6.9	0	0	1.1
9	Nb ₂ O ₅ · nH ₂ O	99	36	15.8	0.9	0	19.3
10	NbOPO ₄	99	75	47.2	5.3	0.5	22.0
11	HZSM-5(0.04/1)	60	81	29.2	9.3	9.2	33.3
12	NbAlS-1(0.027/0.04/1)	60	100	92.3	0.3	0	7.4
13	HZSM-5(0.027/1)	30	73	22.2	6.3	6.7	37.8
14	HZSM-5(0.04/1)	30	76	23.2	4.7	7.1	41.0
15	HZSM-5(0.067/1)	30	85	23.3	4.6	7.4	49.7
16	NbAlS-1(0.027/0.04/1)	30	100	99.3	0	0	0.7
17	Nb ₂ O ₅	30	11	10.1	0	0	0.9
18	Nb ₂ O ₅ · nH ₂ O	30	38	20.0	2.3	0	15.7
19	NbOPO ₄	30	88	78.3	0	0	9.7

^aReaction conditions: catalyst, 2.0 g; reaction temperature, 320 °C; atmospheric pressure; Weight Hourly Space Velocity (WHSV), 0.18 h⁻¹; time-on-stream = 10 h.

^bOther products include C₂-C₄ hydrocarbons (except butene); pentenoic acid isomers; 1-(2-methylcyclopropyl)-ethanone; 3,3-diethoxy-1-propyne; cyclobutanecarboxylic acid-2-propenyl ester; 3-methyl-2-butenic acid, cyclobutyl ester (the latter four compounds are mainly for Entries 4 and 5); 4-ethyl-4-methyl-2-cyclohexene-1-one (detected for Entries 9, 10, 18 and 19); 3-ethyl-1-isopropyl-1H-indene (detected for Entries 10 and 19) and polycyclic aromatics.

Graphic abstract