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Introduction

In many respects, light alkenes comprise the foundation of the petrochemical industry. They are a remarkably versatile industrial feedstock, and proven upgrading strategies can readily transform them into transportation fuels, plastics, and commodity chemicals.¹⁻⁷ Considering the diverse value chains they enable, light alkenes are attractive intermediate targets in biomass refining, where paradigms are frequently based upon coupling small, reactive molecules.⁸ Potentially, light alkenes can be derived from biomass using a number of different technologies, such as ethanol or butanol dehydration,^{9,10} pyrolysis oil upgrading,¹¹ or syngas-based technologies leveraging either Fisher-Tropsch chemistry¹²⁻¹⁵ or methanol synthesis.¹⁶⁻¹⁸ Alternatively, alkenes can be produced via acid-catalyzed decarboxylation of cyclic lactones or alkene-acids.^{19–21} Of this latter category, γ -valerolactone is perhaps the most likely candidate for production in a biorefinery since it is readily derived through hydrogenation of levulinic acid, 2^{2-36} which can be produced from both C₅ and C₆ sugars present in lignocellulosic biomass.^{37–41}

An examination of the intrinsic activity and stability of various solid acids during the catalytic decarboxylation of γ -valerolactone

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Rates of γ -valerolactone (GVL) decarboxylation were measured in the gas phase under anhydrous conditions from 523–723 K over a series of solid acids including amorphous silica alumina, MFI zeolites, supported phosphotungstic acid, and γ -Al₂O₃. Through consideration of decarboxylation rates obtained under differential conditions, we examine the roles of Brønsted and Lewis acidity, deprotonation energy, and catalyst morphology in defining the intrinsic activity and stability of each material. In aluminosilicates, Brønsted sites associated with framework aluminum appear to contribute the majority of decarboxylation activity. Of the aluminosilicates tested, Brønsted sites in MFI are more intrinsically active than analogous sites in ASA; however, zeolite micropores hinder GVL diffusion and lead to mass transfer limitations at high temperatures. Relative to bridging hydroxyls, coordinatively unsaturated aluminum sites are substantially less active and do not contribute significantly to decarboxylation rates in materials having both framework and extraframework aluminum. Decarboxylation barriers scale with the deprotonation energy of Brønsted acid sites; however, lower deprotonation energies do not necessarily imply higher intrinsic activity in GVL decarboxylation. At 623 K, catalyst stability is highest in materials having large pore dimensions, Lewis sites as primary catalytic centers, and Brønsted sites with relatively high deprotonation energies.

> Broadly, GVL decarboxylation over solid acids can occur directly from GVL or proceed through intermediate formation of pentenoic acids, and it yields butene isomers and carbon dioxide (Fig. 1). Prior reports have demonstrated that a number of materials, including amorphous silica-alumina (ASA), γ -Al₂O₃, and WO₄²⁻/Al₂O₃ all catalyze the reaction.¹⁹⁻²¹ Although the transformation was originally proposed to be Brønsted-mediated in ASA,²⁰ Wang and Dumesic have recently shown that GVL decarboxylation also occurs over Lewis-acid sites in γ -Al₂O₃.²¹ By varying Brønsted and Lewis site densities, the authors effected control of alkene distributions obtained through decarboxylation. Specifically, Lewis acid sites allow GVL decarboxylation but are less active for secondary butene isomerization (in the presence of water). In contrast, Brønsted sites promote both decarboxylation and (to a larger extent) alkene isomerization subsequent to decarboxylation. For this reason, relatively Brønsted-rich materials, such as ASA, are slightly more active but deliver an equilibrium-controlled mixture of butene isomers, whereas Lewis-rich materials allow selective production of linear alpha olefins (LAOs).²¹ The observation that Brønsted and Lewis sites appear to catalyze unique decarboxylation pathways motivates consideration of the extent to which each site contributes in materials like ASA, which have significant quantities of both framework and extraframework aluminum. A detailed understanding of decarboxylation at each site could facilitate insightful design of



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Fig. 1 Illustration of the proposed GVL decarboxylation pathway occurring over solid acids. Figure adapted from ref. 19.

materials with, for example, complementary Brønsted and Lewis functionalities to target specific aspects of decarboxylation. In this context, it is additionally important to consider the roles of other parameters, such as Brønsted site deprotonation energy and the local environment of the acid site, which can influence intrinsic activity and provide additional parameters for tuning decarboxylation activity.^{42–46} Finally, prior studies have indicated that solid acids employed during GVL decarboxylation deactivate due to coke formation with time on stream.²⁰ Deactivation can be mitigated to some extent through a steam co-feed in decarboxylation reactors;⁶ however, stability may also correlate with specific physicochemical properties of solid acids such that it can be introduced by design once governing relationships are established.

To address these questions, we have considered the activity and stability of a range of solid acids including γ -Al₂O₃, which is generally considered to be Lewis acidic;^{47,48} ASA, which is amorphous, mesoporous, and has both Brønsted sites associated with framework aluminum and Lewis sites associated with extraframework aluminum;^{49,50} several crystalline, high silica, MFI zeolites that are microporous and primarily exhibit Brønsted sites associated with framework aluminum;^{42,50–52} and a supported heteropolyacid (phosphotungstic acid, PWA), which displays Brønsted sites that should deprotonate readily compared to the above described bridging hydroxyls in ASA and MFI.⁵³ Samples selected also have a range of physicochemical properties, allowing us to probe their effects on both activity and stability.

Materials and methods

Reagents

Sodium metasilicate (Sigma-Aldrich), sodium aluminate (Sigma-Aldrich), sulfuric acid (95.0–98.0%, Sigma-Aldrich),

ammonium sulfate (>99%, Acros), phosphotungstic acid hydrate (Reagent grade, Sigma-Aldrich), ethanol (99.99%, Pharmco-AAPER), and amorphous silica (>99%, Davisil Grade 633, 200-425 mesh, Sigma-Aldrich) were employed for catalyst syntheses. Prior to use in kinetic studies, γ -valerolactone (GVL, >98%, Sigma-Aldrich) was dried over silica gel (5% w/v, 12-24 mesh, Strem Chemicals).⁵⁴ 4-Pentenoic acid (97%, Sigma-Aldrich), 3-trans-pentenoic acid (95%, TCI America), 2-pentenoic acid (98%, Sigma-Aldrich), 1-butene (0.1% in He, Scott), propylene (1% in He, Praxair), and CO₂ (5% in N₂, Airgas) were used as supplied by the manufacturers for standard preparation and instrument calibration. Isopropylamine (IPA, 99%, Acros) and pyridine (>99.0%, Sigma-Aldrich) were used as probe adsorbates for acid site titration. IPA was used without purification, and pyridine was dried over potassium hydroxide (85% Acros).55 Purified water used in sample preparation was prepared in house by sequential reverse osmosis, UV oxidation, and double deionization. He (99.999%, Airgas), N₂ (99.999%, Airgas), and Air (Medical Grade, Airgas) were used in multiple applications as described in subsequent sections. To eliminate water adsorption during FTIR sample preparation, we employed purge gas generated in-house from dried compressed air (-70 °C Dew Point, Peak Scientific) for catalyst pretreatment (e.g., calcination).

Catalyst preparation

Five amorphous silica-alumina (ASA) samples were considered in this study, and each is identified using the convention ASA-XXX.x, where the variable portion of the label specifies the atomic ratio of silicon to aluminum in that sample. ASA-005.3a and ASA-05.3b were supplied by Grace-Davison (SIAL 3113 and 3901, respectively), while ASA-067.6, ASA-004.4, and ASA-002.0 were synthesized using a co-gelation procedure.⁵⁶ For all synthesized ASA samples, aqueous solutions of sodium metasilicate and sodium aluminate were combined in desired molar ratios, resulting in gel formation. The gel was then aged for 30 minutes at 339 K before decreasing the solution pH to 9 using a 10 wt% aqueous solution of sulfuric acid. Recovered solids were then washed with deionized water, dried at 398 K, and ion exchanged using aqueous ammonium sulfate (10% w/v). Ammonium-exchanged ASA samples were recovered by filtration, washed with deionized water to remove residual sulfates, dried in air at 398 K, ground to a uniform particle size, and calcined in air (100 ml min⁻¹, 773 K, 4 h, 3 K min⁻¹) to obtain H⁺ form ASA. Prior to use, commercial ASA samples were calcined using an identical protocol but were not otherwise modified.

MFI samples of varied aluminum content were obtained from commercial suppliers. This family of analogs is designated using the convention MFI-XXX.x, where the variable portion of the label specifies their atomic ratio of silicon to aluminum. MFI-500.0 (Acros), MFI-200.0, (Alfa Aesar), MFI-080.0 (Alfa Aesar), and MFI-030.0 (Alfa Aesar) were supplied in either H⁺ or ammonium form. Prior to use, all MFI samples were calcined in flowing air (100 ml min⁻¹, 4 h, 773 K, 3 K min⁻¹).

 γ -Al₂O₃ (Strem) was calcined (100 ml min⁻¹,4 h, 773 K, 3 K min⁻¹) prior to use. Supported phosphotungstic acid (PWA) was prepared by impregnation of phosphotungstic acid hydrate dissolved in ethanol onto amorphous silica as required to achieve desired PWA loadings. PWA/SiO₂ samples were subsequently sealed in a vial, aged for 12 hours at ambient temperature, dried in an oven at 393 K, and treated in flowing air (100 ml min⁻¹, 4 h, 623 K, 3 K min⁻¹).^{44,53}

Catalytic activity testing

GVL decarboxylation was carried out in a gas phase, downflow reactor. The apparatus is illustrated in Fig. 2. Catalyst samples were loaded into a 316 stainless steel tube having either a 1/4" or 1/2" outer diameter as required to minimize pressure differentials with varied catalyst loadings. Catalyst beds were held in the reactor with quartz wool end plugs, and bed lengths were generally 1-3 cm. Dead volume upstream and downstream of the catalyst bed was packed with fused silica granules (850-2000 µm, 99.9%, Sigma-Aldrich), and each end of the reactor was capped with a plug of quartz wool. The reactor was mounted inside an aluminum block within an insulated furnace (Applied Test Systems). Reactor temperature was monitored using a Type K thermocouple (Omega) positioned against the exterior reactor wall at the center of the catalyst bed, and temperature was regulated using a PID controller (Omega CN7500). Prior to introducing reactant feeds to packed beds, catalyst samples were calcined *in situ* under flowing air (50 ml min⁻¹) using protocols described in the catalyst preparation section.

Neat GVL was fed into the apparatus at ambient temperature using a syringe pump (0.05 ml min⁻¹, Cole-Parmer,



Fig. 2 Schematic of experimental apparatus used in measuring GVL decarboxylation rates over various solid acids.

model 110). The liquid feed was vaporized in a temperatureregulated gas-liquid contactor by combining with a He stream (50 ml min⁻¹) controlled by mass flow controller (Brooks, 5850S). The combined GVL/He stream (19.0 mol% GVL) was then preheated to reaction temperature. In typical operation, the catalyst bed was bypassed until steady-state GVL concentrations were observed in the feed stream, at which point the combined feed was diverted into the reactor inlet. The reactor effluent was sent to a vapor-liquid separator (298 K), where low vapor pressure species (GVL and PEA isomers) were condensed, diluted in water, and quantified using a GC-FID (GC 7890A, Agilent) equipped with an Innowax column. Decarboxylation products (butene isomers, CO_2) were retained in the vapor phase and sent to an in-line gas chromatograph (GC 7890A, Agilent) equipped with separate injectors, columns, and detectors for hydrocarbon and CO₂ analysis. Butenes were resolved using an HP-PONA column, and their concentrations were determined via calibrated FID response. CO2 was resolved using a HP-PLOT/Q column and quantified via TCD response relative to a helium reference.

For all experiments summarized here, reactors operated differentially (<4% GVL conversion), and the only reaction products observed were butenes, CO_2 , and pentenoic acid isomers. As such, we assume that GVL partial pressures do not change significantly across the bed. Further, we assume that product partial pressures (pentenoic acids, butene, and CO_2) remain sufficiently close to zero such that their bulk

concentrations do not strongly influence the kinetics of GVL decarboxylation. We note that this does not exclude the possibility that decarboxylation can occur through intermediate formation of pentenoic acid; it only implies that the bulk concentration of pentenoic acid isomers remains low throughout the catalyst bed. Carbon balances based on combined analysis of gas and liquid phases typically closed to within 5%. Since conversion ranges for differential operation are within the precision range expected of mass balance closure and GC analysis, GVL conversion was determined based on product formation as defined in eqn (1), where n_{C4} and n_{PEA} are the total molar quantities of butenes and pentenoic acids recovered in a given time period, and n_{GVL0} is the total molar quantity of GVL fed into the system in the same time period.

$$X_{\rm GVL} = \frac{n_{\rm C4} + n_{\rm PEA}}{n_{\rm GVL_0}} \tag{1}$$

Intensive rates of reaction are presented here on both mass-normalized and acid site-normalized bases (*i.e.*, turn-over frequencies, TOF). Mass normalized rates of reaction are calculated from measured butene production rates according to eqn (2).

$$r_{\rm DC} = \frac{R_{\rm C4}}{m_{\rm cat}} \tag{2}$$

Where R_{C4} represents the extensive butene production rate determined by GC analysis, and m_{cat} is the total mass of catalyst in the bed. TOFs are reported on either a Brønsted or Lewis site basis. In either case, they are calculated by dividing the mass-normalized rate of decarboxylation by the molar density of Brønsted or Lewis sites in a given catalyst (see Catalyst characterization section). TOFs reported here have units of moles butene per mole of acid site per minute, which is expressed as min⁻¹ for convenience. All of the solid acids tested deactivate when first placed on stream, yet all of the characterization methods we have employed describe the catalyst in a pristine state. To facilitate meaningful comparison between unique sites in different materials, all kinetic data summarized here represent theoretical decarboxylation rates at zero time on stream. These were estimated by regression of decaying decarboxylation rates as a function of time.

Decarboxylation of GVL does occur over quartz packing at temperatures above 573 K. Accordingly, background decarboxylation rates were measured in both 1/4" and 1/2"stainless steel tubes packed with quartz granules at all temperatures where kinetic data are reported here. In all cases, we observed that background activity does not contribute significantly to extensive butene production rates measured in the presence of catalyst beds. Specifically, for ASA, MFI, and PWA samples, background GVL decarboxylation rates were less than 1% of the extensive butene production rates at all temperatures considered. For γ -Al₂O₃, background GVL decarboxylation rates were less than 3% of the extensive butene production rates at all temperatures considered.

Catalyst characterization

All materials were characterized by physisorption of N_2 at 77 K (Micromeritics ASAP 2020). Prior to N_2 dosing, samples were outgassed under vacuum (623 K, 4 h). Total and micropore surface areas were determined by BET and *t*-plot analyses, respectively. Pore diameters for mesoporous samples were determined from BJH analysis of the desorption branch of N_2 uptake isotherms.⁵⁷ Pore dimensions for microporous samples were determined using the Saito–Foley modification to the Horvath–Kawazoe method.⁵⁸ Pore volumes were estimated from the cumulative amount of nitrogen uptake at a relative pressure of 0.995.

Brønsted site densities were determined from molar quantities of propylene evolved between 575 K and 700 K during temperature programmed desorption (TPD) of isopropylamine (IPA).⁵⁹ Approximately 100 mg of powdered catalyst were loaded into a quartz tube (1/4") with a fritted distension (1/2") in the center, and the tube was positioned in a high temperature furnace (Omega) and connected to a gas flow manifold. Prior to analysis, catalysts were calcined in situ according to standard protocols (see above Catalyst preparation section), cooled to 296 K, and purged (60 ml min⁻¹) with He that was dried over molecular sieves. After pretreatment, the sample was held at 296 K and contacted for 60 minutes with an IPA/He blend prepared by flowing He (60 ml min⁻¹) through the headspace of an IPA saturation chamber held in an ethanol/liquid nitrogen bath. The cell was then purged with He (296 K, 60 min) and subsequently ramped to 873 K (10 K min⁻¹). During the temperature ramp, the cell effluent was monitored using a mass selective detector (Stanford Instruments RGA 100). Signals corresponding to IPA (m/z = 44) and propylene (m/z = 41) were monitored continuously, and Brønsted site densities were calculated from evolved propylene based on the assumption that one molecule of propylene forms at one accessible Brønsted site.

Relative quantities of Brønsted and Lewis sites were determined using transmission FTIR spectroscopy (Nicolet 6700, DTGS detector) of adsorbed pyridine on catalyst samples. Catalysts were pressed into self-supporting wafers (10–15 mg catalyst, 13 mm diameter, 0.5–5 tons force), loaded into an aluminum sample holder, and positioned in a glass flow cell having separate zones for spectral acquisition and sample pretreatment. Samples were pretreated in an externally heated, temperature-controlled zone positioned directly above the spectral acquisition zone. Spectra were acquired from samples positioned at the center of an unheated glass tee sealed with CaF_2 end caps, and the sample holder was vertically mobile to permit transfer of samples between the two sections.

In a typical pyridine adsorption experiment, samples were calcined in purge gas (100 ml min⁻¹, 4 h, 723 K, 3 K min⁻¹). Subsequently, the sample was cooled to 423 K, and the cell

was purged under He flow. Prior to introducing into the gas manifold, He was purified in sequential cryogenic and molecular sieve traps to remove trace moisture and hydrocarbon impurities. Under a continuous purge, the sample was lowered into the spectral acquisition section, and a background spectrum was recorded. The sample was then transferred to the heated zone (423 K) and the helium purge flow was switched to a pyridine/He blend prepared by passing He (100 ml min⁻¹) through the head space of a saturator containing dry pyridine and held at 263 K using an NaCl/ice bath. Pyridine was dosed onto the sample (423 K) for 60 minutes, and the sample was subsequently purged with helium (423 K) for another 60 minutes to remove physically adsorbed pyridine. The sample was then lowered into position between the CaF2 windows under a continuous He purge, and a spectrum of adsorbed pyridine was acquired.

Brønsted and Lewis site ratios were determined from difference spectra by integration of IR bands at 1545 cm⁻¹ and 1455 cm⁻¹.⁶⁰⁻⁶² In our analysis, we employed molar extinction coefficients published by Satsuma, which are 1.23 and 1.73 cm μ mol⁻¹ for Brønsted and Lewis sites, respectively.⁶³ For all materials except γ -Al₂O₃, Lewis site densities were estimated based on Brønsted site densities determined from IPA desorption and Brønsted : Lewis ratios measured by FTIR spectra of adsorbed pyridine. In the case of γ -Al₂O₃, we observed no pyridinium ion formation (1545 cm⁻¹) in FTIR, and its Lewis site density was determined directly from FTIR difference spectra of adsorbed pyridine based on the band at 1455 cm⁻¹.

Results and discussion

Catalyst characterization and productivity in GVL decarboxylation

Table 1 summarizes the physical and chemical properties of all catalysts considered here alongside their mass-normalized

rates of GVL decarboxylation (DC rate, 623 K, 0.19 bar GVL) at zero time on stream. For a visual comparison, each catalyst is additionally ranked in order of decreasing DC rates in Fig. 3. In general, the catalyst properties summarized in Table 1 vary according to expectations with *e.g.*, aluminum content and morphology. Since it is outside the focus of this study, we have not pursued a rigorous explanation for the observed increase in Brønsted–Lewis ratio for decreasing Si:Al ratios in low-silica ASA samples, but we speculate that it arises from structural heterogeneity, noting that it is difficult to control the distribution of framework and extraframework aluminum using the co-gelation method employed here. As there is uncertainty in titrating accessible



Fig. 3 Comparison of mass-normalized decarboxylation rates measured over the solid acids documented in Table 1. Decarboxylation rates were measured at 623 K and 0.19 bar GVL at a total system pressure of 1 bar with a helium balance. Weight-hourly space velocities were varied for each catalyst to maintain differential conversions.

Table 1 Summary of physicochemical properties and measured decarboxylation rates of solid acids considered in this study. Decarboxylation rates reported here were measured at 623 K and 0.19 bar GVL at 1 bar system pressure with a helium balance. Weight-hourly space velocities were varied as necessary to maintain differential conversion

| Catalyst | BET surface area $(m^2 g^{-1})$ | Micropore area $(m^2 g^{-1})$ | Pore diameter (Å) | Pore volume (cm ³ g ⁻¹) | Brønsted sites $(\mu mol g^{-1})$ | B:L | DC rate $(\mu mol min^{-1} g^{-1})$ |
|----------------------------------|---------------------------------|-------------------------------|----------------------|---|-----------------------------------|------|-------------------------------------|
| ASA | | | | | | | |
| ASA-067.6 | 550 | 130 | 32 | 0.40 | 52 | 3.0 | 66 |
| ASA-005.3a | 610 | 0.0 | 42 | 0.81 | 340 | 0.34 | 440 |
| ASA-005.3b | 420 | 0.0 | 45 | 0.61 | 105 | 0.47 | 150 |
| ASA-004.4 | 320 | 7.0 | 67 | 0.58 | 180 | 0.64 | 290 |
| ASA-002.0 | 120 | 7.0 | 140 | 0.41 | 63 | 0.96 | 95 |
| MFI | | | | | | | |
| MFI-500.0 | 360 | 100 | 5.3 | 0.22 | 39 | 12 | 230 |
| MFI-200.0 | 360 | 140 | 5.8 | 0.22 | 79 | 13 | 440 |
| MFI-080.0 | 390 | 230 | 5.4 | 0.27 | 320 | 9.6 | 690 |
| MFI-030.0 | 380 | 240 | 5.3 | 0.28 | 560 | 8.7 | 750 |
| Other | | | | | | | |
| γ-Al ₂ O ₃ | 230 | 5.0 | 60 | 0.47 | 70.0 | 0.0 | 1.5 |
| 5% PWA | 470 | 1.0 | 56 | 0.84 | 30 | 0.52 | 7.8 |
| SiO ₂ | 480 | 2.0 | 57 | 0.87 | 0.0 | — | 0.05 |
| | | | | | | | |

Brønsted sites in supported heteropolyacids,⁵³ it is worth commenting on the Brønsted site density measured here for 5% PWA/SiO₂ (30 µmol g⁻¹) by TPD of IPA after calcination in air at 623 K. A site density of 30 µmol g⁻¹ corresponds to roughly 1.7 accessible protons per polyoxymetallate cluster in 5% PWA/SiO₂, which is lower than the theoretically anticipated value of 3.0. This result generally agrees with Brønsted site densities for 5% PWA/SiO₂ reported by Iglesia (1.4–2.9 H⁺ per Keggin unit) using *in situ* titration with pyridine and di-*tert*butyl pyridine under various reaction conditions.^{43,53,64} We thus consider that the Brønsted site density measured here by IPA desorption provides a reasonable basis for calculating turnover frequencies in PWA/SiO₂. Further discussion of specific properties and their impact on activity and stability will be deferred to subsequent sections.

Of the materials tested here, MFI zeolites are, on average, the most active, achieving initial DC rates ranging from 220–750 μ mol min⁻¹ g⁻¹, and DC rates generally increase with aluminum content in MFI. ASA samples are slightly less active than MFI zeolites, demonstrating DC rates ranging from 66–440 μ mol min⁻¹ g⁻¹. Unlike the MFI series, there is no clear correlation between aluminum content and DC rates in the ASA samples. Both 5% PWA/SiO₂ and γ -Al₂O₃ are substantially less active than either MFI or ASA, achieving decarboxylation rates of 7.8 and 1.5 µmol min⁻¹ g⁻¹, respectively, at 623 K and 0.19 bar GVL. From a practical viewpoint, aluminosilicates seem broadly well-suited to GVL decarboxylation based on their high DC rates, and we generally conclude that a high aluminum content benefits overall catalyst productivity. This aligns with the expectation that low Si:Al ratios imply high acid site densities in aluminosilicates; however, this presentation does not delineate contributions from multiple underlying factors. For example, most of the materials summarized in Table 1 have heterogeneous site distributions and display both Brønsted and Lewis acidity. Either

type of site is proposed to catalyze GVL decarboxylation, but contributions from each are not apparent in massnormalized rates.²¹ Further, the local structure and deprotonation energy of Brønsted sites vary among the materials tested, and either may influence reactivity and stability.⁴² In subsequent sections, we decouple these effects to the extent possible to define the intrinsic activity and stability of varying acid sites.

Amorphous silica alumina and γ-Al₂O₃

Examining the ASA data summarized in Table 1, we observe that, despite spanning a considerable range of surface areas (120-610 m² g⁻¹), pore diameters (32-140 Å), and Brønsted : Lewis ratios (0.3-3.0), mass-normalized DC rates in ASA depend only on the Brønsted site density of a particular sample. This conclusion is emphasized in Fig. 4a, which illustrates decarboxylation rates plotted against Brønsted site counts on a logarithmic scale. Linear regression of this data set reveals a slope of 0.99 ± 0.21 , indicating that DC rates in ASA have a first order dependence on Brønsted site density. This observation allows the conclusion that the Koros-Nowak criteria are rigorously satisfied for this ASA series at 623 K.^{65,66} Thus, rates observed over each ASA sample reflect kinetic control; the intrinsic DC activities of Brønsted sites in ASA do not vary with aluminum content; and Brønsted sites in each ASA sample are described by a single turnover frequency.

As illustrated in Fig. 4b, DC rates over ASA at 623 K are well-described by a line having a slope of $1.36 \pm 0.13 \text{ min}^{-1}$ and passing through the origin. The calculated slope represents the average TOF of a Brønsted site in ASA, and a zero-intercept implies that, in the absence of Brønsted sites, no decarboxylation activity is expected in ASA. This result is consistent with our observation that amorphous SiO₂, which



Fig. 4 Illustration of the relationship between mass-normalized decarboxylation rates and Brønsted site density measured over ASA samples of varying aluminum content at 623 K and 0.19 bar GVL at 1 bar total pressure in a helium balance. (\odot) ASA-067.6, (\triangle) ASA-002.0, (\Box) ASA-005.3b, (\diamond) ASA-004.4, (∇) ASA-005.3a. a) Display of linearity in fulfillment of Koros-Nowak criteria for illustration of kinetic control during GVL decarboxylation in ASA. b) For ASA samples of varying Brønsted : Lewis ratios, decarboxylation rates depend only on the Brønsted site density at 623 K. In both Fig. a and b, decarboxylation rates are reported in µmol min⁻¹ g⁻¹ and H⁺ site densities are reported in µmol g⁻¹.

displays no Brønsted signatures in pyridine FTIR or IPA TPD, shows little activity during GVL decarboxylation at 623 K ($0.05 \ \mu mol \ min^{-1} \ g^{-1}$). No significant deviation from the illustrated trend is evident in the ASA samples despite considerable variation in Brønsted: Lewis ratio (0.3-3.0), indicating that GVL decarboxylation is insensitive to Lewis sites in ASA.

Consistent with prior observations by Wang and Dumesic,²¹ decarboxylation activity was observed here above background levels at 623 K and 0.19 bar GVL over y-Al₂O₃ (1.5 μ mol min⁻¹ g⁻¹); however, it is substantially lower than analogous rates in ASA. Tentatively, the low activity of γ -Al₂O₃ could be attributed to weakly (Brønsted) acidic surface hydroxyls, coordinatively unsaturated (Lewis) aluminum sites, or unanticipated acidity arising from residual impurities. As in prior spectroscopic studies of pyridine adsorption, we observe appreciable Lewis acidity but no clear pyridinium ion formation on γ-Al₂O₃, suggesting a catalyst without Brønsted acidity.^{47,48} However, we did observe roughly 70 μ mol g⁻¹ of propylene evolution from γ -Al₂O₃ during IPA TPD, suggesting at least a modest surface density of Brønsted sites. As to the nature of the Brønsted sites detected by IPA desorption, we speculate that it is likely attributed to residual impurities rather than surface hydroxyls associated with aluminum since the latter have been demonstrated by Gorte to not catalyze IPA deamination.⁴⁷ As such, the DC activity of γ -Al₂O₃ reported here is most likely attributed either to Brønsted acidity conferred by residual impurities or to a Lewis-mediated decarboxylation pathway, with prior studies by Dumesic supporting the role of Lewis acidity.²¹ Based on FTIR spectra of adsorbed pyridine on γ -Al₂O₃, we estimate a Lewis-site density of roughly 148 µmol g⁻¹. If DC activity is attributed to coordinatively unsaturated aluminum sites in γ -Al₂O₃, they appear to have a turnover frequency of 0.01 min⁻¹ and are thus two orders of magnitude less active than bridging hydroxyls in ASA. If this turnover frequency is taken as representative of the intrinsic activity of Lewis sites in ASA, we calculate (from Table 1) that Lewis sites contribute anywhere from 0.2-2.2% of the initial

GVL decarboxylation rate in ASA samples, and that Brønsted sites account for the remainder. This estimate is consistent with the trend in Fig. 4b, which indicates that DC rates depend only on Brønsted site counts in ASA.

Previously, Wang and Dumesic reported a steady state decarboxylation rate of 12 μ mol min⁻¹ g⁻¹ at 673 K for the decarboxylation of pentenoic acid over γ -Al₂O₃ under anhydrous conditions (0.07 bar PEA in He), which agrees well with a steady state rate of 10 μ mol min⁻¹ g⁻¹ measured here for GVL decarboxylation over γ -Al₂O₃ at 673 K (0.19 bar GVL in He). In prior studies, when the helium balance was replaced with water, a five-fold enhancement in decarboxylation rates is observed over γ -Al₂O₃, while less pronounced²¹ or inhibitory²⁰ effects are observed over ASA. This result suggests that water uniquely promotes decarboxylation pathways at coordinatively unsaturated aluminum centers and that Lewis-catalyzed decarboxylation may comprise a larger portion of total butene production rates in the presence of water.

MFI

In contrast to ASA samples, mass normalized decarboxylation rates over MFI samples of varied aluminum content do not correlate uniformly with Brønsted site density at 623 K (Fig. 5a). Rather, we observe that production rates appear to scale directly with Brønsted site density only in the highest silica samples (Si:Al > 80). Thereafter, increases in DC rates diminish with further increases in aluminum content, and the MFI series approaches an overall maximum production rate of roughly 750 µmol min⁻¹ g⁻¹ at 623 K in the MFI-030.0 sample. This leads to the conclusion that turnover frequencies in MFI decrease with aluminum content, and we consider that both kinetic and transport phenomena may underlie this observation.

Based on available data for γ -butyrolactone and ϵ -caprolactone, GVL has an approximate kinetic diameter between 5.0 and 6.0 Å (calculated based on critical molar



Fig. 5 Illustration of the relationship between mass-normalized decarboxylation rates and Brønsted site density measured over MFI zeolites of varying aluminum content at 623 K and 523 K, 0.19 bar GVL, and 1 bar total pressure in a helium balance. MFI-500.0 (\diamond), MFI-200.0 (\Box), MFI-080.0 (∇), MFI-030.0 (\bigcirc) a) 623 K b) 523 K.

volumes as per Jae⁶⁷), which is on the same order as the average pore size of the MFI samples employed here (5.5 Å). It is thus reasonable to expect that pore access and diffusion of GVL are hindered in MFI compared to mesoporous ASA. Further, MFI-080.0 and MFI-030.0 have relatively high areal densities of Brønsted sites (0.80 and 1.46 µmol m⁻², calculated from Table 1) compared to the most Brønsted-dense ASA samples, ASA-005.3a and ASA-004.4 (0.55 and 0.57 μ mol m⁻²). The combination of a high surface density of acid sites coupled with small pore diameters suggests that diffusion limitations could be significant in MFI despite not being observed in ASA. Increasing mass transfer limitations at higher site densities would explain the trend illustrated in Fig. 5a; however, this conclusion discounts the possibility that Brønsted sites in MFI zeolites are nonequivalent in the range of Si: Al ratios tested here. Although Brønsted sites in high-silica MFI (*i.e.*, Si:Al > 10) should display uniform deprotonation energies, framework aluminum atoms can occupy a range of tetrahedral sites and local environments in the MFI framework.⁵² As previously described by Gounder, the nanoscale effects of confinement and solvation frequently control reactivity in zeolites; thus, it is possible that heterogeneous distributions of framework aluminum in MFI could lead to actual variations in intrinsic activity as opposed to apparent ones arising from transport limitations.⁶⁸ Rigorous consideration of diffusion limitations in this system is therefore warranted, and relevant data supporting this discussion is summarized in Fig. 6, which illustrates observed trends in DC rates over MFI zeolites as a function of Brønsted site density at 523 K and 623 K.

Regression of the high temperature data set (623 K) in Fig. 6 indicates a slope of 0.43 ± 0.16 . Assuming structure insensitivity in GVL decarboxylation over MFI, this result suggests that internal diffusion controls the rate of decarboxylation in MFI at 623 K. To probe the possibility that site heterogeneity could lead to decreasing turnover frequencies



Fig. 6 Correlation between decarboxylation rates and Brønsted site densities in MFI at 623 K (open symbols) and 523 K (filled symbols). MFI-500.0 (\diamond), MFI-200.0 (\Box), MFI-080.0 (∇), MFI-030.0 (\odot). Decarboxylation rates are reported in μ mol min⁻¹ g⁻¹ and H⁺ site densities are reported in μ mol g⁻¹.

with increasing aluminum content, DC rates were measured at 523 K under otherwise identical conditions, with the reasoning that a 100 K decrease in temperature should affect DC rates and GVL diffusion to different extents and thus permit discrimination between kinetic and transport effects. As illustrated in Fig. 6, regression of the low temperature data set indicates a slope of 0.84 ± 0.34 , suggesting that DC rates over MFI are shifted toward kinetic control at 523 K.⁵⁷ This is consistent with the interpretation that mass transfer, rather than varying intrinsic activity, is the source of apparent decreasing turnover frequencies with increasing aluminum content in MFI zeolites at 623 K. Emphasizing this point, Fig. 5b shows that decarboxylation rates over MFI at 523 K vary linearly with Brønsted site density and are captured by a line passing through the origin. Thus, Brønsted sites in MFI are the primary catalytic centers for GVL decarboxylation, and they appear to be equivalent in this context over a broad range of Si: Al ratios (30-500).

Since kinetic control is not rigorously demonstrated for all MFI samples at 623 K, we are cautious in defining a turnover frequency for MFI at this temperature; however, based on the trend illustrated in Fig. 5a, a meaningful comparison between MFI and ASA can be established. Specifically, Fig. 5a illustrates that the linear trend in decarboxylation predicted by the MFI-500.0 and MFI-200.0 samples does extrapolate to the origin. This suggests that at low aluminum contents, there is a first order relationship between decarboxylation activity and Brønsted site density, i.e., the data represent kinetic control. Based on the regression illustrated in Fig. 5a (which includes the background level activity of amorphous silica), we estimate that Brønsted sites in MFI have a DC turnover frequency of $5.54 \pm 0.36 \text{ min}^{-1}$ at 623 K and are thus roughly four times more intrinsically active than analogous sites in ASA (1.36 min^{-1}).

The kinetic effects of acid site variation

We have thus far demonstrated that GVL decarboxylation over aluminosilicates appears relatively insensitive to Lewis acidity such that overall activity in anhydrous environments is determined by the intrinsic activity and total number of characteristic Brønsted sites. Despite having Brønsted sites with comparable deprotonation energies ($\approx 1200 \text{ kJ mol}^{-1}$),⁴² MFI and ASA present turnover frequencies that differ by a factor of four, and we explore the source of this discrepancy in this section. We further compare the activity of ASA and MFI to that of 5% PWA/SiO₂, which has Brønsted sites characterized by a significantly lower deprotonation energy (DPE = 1050–1100 kJ mol⁻¹) than either of the aluminosilicates.^{42,64} We additionally expand our consideration of γ -Al₂O₃ to improve our understanding of its relatively low activity in GVL decarboxylation.

For PWA/SiO₂, reference experiments were carried out under differential conditions at 623 K with samples having both 5 wt% and 20 wt% PWA. Over these two catalysts, we observed equivalent, Brønsted-normalized turnover frequencies, suggesting that mass transfer limitations are absent during GVL decarboxylation over PWA/SiO₂ at 623 K. We did not test explicitly for internal diffusion limitations in γ -Al₂O₃; however, its pore dimensions are comparable with the ASA series (~50 Å) and its mass-normalized decarboxylation rate (1.5 µmol min⁻¹ g⁻¹, 623 K) is 2 orders of magnitude smaller than ASA, on average. Since kinetic control was rigorously demonstrated in the ASA series at 623 K, we assume that this conclusion extends to the less reactive γ -Al₂O₃.

Calculated turnover frequencies (623 K, 0.19 bar GVL) for each material are summarized in Fig. 7. The most active sites under the conditions tested appear to be protons in MFI (5.54 min⁻¹) and ASA (1.36 min⁻¹). Brønsted sites in 5% PWA/SiO₂ display a substantially lower turnover frequency (0.26 min⁻¹) than either of the aluminosilicates. This suggests that a more easily deprotonated acid site does not necessarily imply a more active catalyst during GVL decarboxylation and may point to the significance of structural effects in this reaction. It is worth mentioning that Keggin structures swell to varying extents depending on the titrant and reaction environment, and it is possible that protons in PWA/SiO₂ are more or less accessible to GVL than they are to IPA. There is thus uncertainty in our apparent TOF. In the event that protons in the Keggin structure are substantially less accessible to GVL than they are to IPA, Brønsted sites in PWA/SiO₂ could be significantly more active than indicated by the values reported here. As described earlier, decarboxylation over γ -Al₂O₃ is most likely attributed to Lewis sites, and we have accordingly calculated its turnover frequency on this basis to be roughly 0.01 min⁻¹, indicating it is the least intrinsically active of the materials considered here.

For a more comprehensive view, Fig. 8 presents Arrhenius plots for the four materials compared in this section: MFI-500.0, ASA-005.3a, 5% PWA/SiO₂, and γ -Al₂O₃. For each



Fig. 7 Initial turnover frequencies measured under differential conditions over MFI, ASA, 5% PWA/SiO2, and γ -Al₂O₃ at 623 K and 0.19 bar GVL at 1 bar total pressure in a helium balance. For MFI and ASA, estimated turnover frequencies reflect the average of samples for which kinetic control has been demonstrated. The turnover frequency indicated for γ -Al₂O₃ is calculated on a Lewis site basis. All other turnover frequencies are calculated on a Brønsted site basis.



Fig. 8 Arrhenius plots illustrating the temperature dependence of GVL decarboxylation over γ -Al₂O₃ (\circ), PWA/SiO₂ (\Box), ASA-005.3a (x), MFI-500.0 (\diamond). Decarboxylation turnover frequencies reported here have units of min⁻¹.

sample, kinetic rate control has been adequately demonstrated at 623 K and below. Rate data were additionally collected at higher temperatures, but we note no deviation from low-temperature trends in high-temperature data, permitting the assumption that where higher temperature data are reported, they also reflect kinetic control. Arrhenius parameters for each material are summarized alongside calculated turnover frequencies in Table 2. In this presentation, both pre-exponential factors and activation barriers are apparent and reflect lumped contributions from multiple elementary phenomena.

 γ -Al₂O₃ has the highest decarboxylation barrier of any material tested (172 kJ mol⁻¹), which aligns with its relatively low intrinsic activity. Whether its catalytic activity is attributed to coordinatively unsaturated aluminum or trace impurities, either type of site appears to facilitate a higher energy decarboxylation pathway than catalysts that have a more pronounced Brønsted character. This is consistent with the results of preceding sections that suggest extraframework aluminum contributes little to the catalytic activity of aluminosilicates in the absence of water. MFI and ASA have essentially indistinguishable apparent activation barriers of 138 and 130 kJ mol⁻¹. This could indicate that DC barriers over Brønsted sites are largely controlled by their deprotonation energy, which should be comparable (≈ 1200 kJ mol⁻¹) in these two materials.⁴² Supporting this conclusion, we

Table 2 Apparent Arrhenius parameters measured for MFI-500.0, ASA-005.3a, 5% PWA/SiO₂, and γ -Al₂O₃. Turnover frequencies were measured under differential conditions at 623 K and 0.19 bar GVL and 1 bar total pressure in a helium balance. Errors in apparent activation barriers were determined at a 95% confidence level

| Catalyst | $A(\min^{-1})$ | $E_{\rm A} \left({\rm kJ} \ {\rm mol}^{-1} \right)$ | $\pm (kJ mol^{-1})$ | TOF (min ⁻¹) |
|--|---------------------|--|---------------------|--------------------------|
| MFI-500.0 | $2.6 	imes 10^{12}$ | 138 | 13 | 5.54 |
| ASA-005.3a | $6.4 	imes 10^{10}$ | 130 | 24 | 1.36 |
| PWA/SiO ₂ | $1.3 	imes 10^7$ | 92 | 10 | 0.26 |
| γ -Al ₂ O ₃ | $1.7 	imes 10^{12}$ | 172 | 36 | 0.01 |
| | | | | |

observe a substantially lower DC barrier over 5% PWA/SiO_2 (92 kJ mol⁻¹), which has Brønsted sites characterized by a significantly lower deprotonation energy (1050–1100 kJ mol⁻¹) than what is commonly reported for aluminosilicates.⁴²

Despite the fact that measured barriers appear to scale with deprotonation energy, decarboxylation activity is not necessarily anticipated by observed activation barriers. Specifically, ASA and MFI have comparable barriers, but their turnover frequencies vary by a factor of four. In contrast, DC barriers are relatively low over 5% PWA/SiO₂, but Brønsted sites therein display a diminished turnover frequency (0.26 min⁻¹) compared to either MFI (5.54 min⁻¹) or ASA (1.36 min⁻¹). Examining the pre-exponential factors given in Table 2, we observe that the differences in activity between MFI, ASA, and PWA/SiO₂ are captured by the magnitude of their prefactors; however, it is difficult to interpret this result with further resolution. First, the variability in Arrhenius parameters observed here is large and arises from the relative imprecision of collecting kinetic data in deactivating systems. At 623 K and assuming a common pre-exponential factor for all materials, variation of barriers within the indicated precision could explain the majority of observed differences in turnover frequencies. Further, since no detailed microkinetic description of GVL decarboxylation has been established, concentration dependencies here are lumped into the preexponential factor. We have previously observed GVL decarboxylation to be zero-order in GVL over ASA,²⁰ but this has not been rigorously extended to MFI, PWA/SiO₂, and γ -Al₂O₃. Finally, we have already noted the uncertainty in determining accurate, Brønsted-normalized TOFs for PWA/SiO₂ using TPD of IPA, and this uncertainty is similarly lumped into the preexponential factors reported here. Given the high temperature nature of this reaction (523-723 K), entropic effects may indeed be significant in defining the intrinsic activity of a catalyst; however, multiple other factors could additionally underlie the observed variations. Brønsted sites with lower

deprotonation energies do appear to have reduced barriers for GVL decarboxylation, but the extent to which deprotonation energy or other factors (*e.g.*, confinement) control the intrinsic activity of an acid site remains unclear.

Catalyst stability

Fig. 9 illustrates the activity of selected materials as a function of time on stream. Here, dimensionless activity is calculated by normalizing decarboxylation rates measured over a given catalyst at the indicated time on stream by the decarboxylation rate for the same catalyst at zero time on stream. Fig. 9a compares MFI-500.0 to two ASA samples at 623 K, providing a comparison of materials having Brønsted sites with comparable deprotonation energies but different physical properties (Table 1). Fig. 9b compares ASA-005.3a, 5 wt% PWA/SiO₂, and γ -Al₂O₃ at 623 K to highlight stability differences between materials having comparable physical properties (Table 1) but varying acid sites and decarboxylation barriers. In each case, deactivation is attributed to coke formation based on color change in spent samples, and all catalysts lose activity with time on stream. A rigorous comparison of catalyst stability is difficult because each material displays unique, non-integer deactivation orders, and we were not able to capture the on-stream activity of each sample with a single deactivation model. However, at short times on stream (<30 min), all deactivation profiles exhibit pseudo-first order kinetics. We therefore estimated first order deactivation constants from initial periods on stream to allow a quantitative comparison of catalyst stability. Deactivation constants are presented alongside potentially relevant physical and chemical properties in Table 3.

From Fig. 9a, it is apparent that the stability of the aluminosilicates decreases in the order ASA-005.3a > ASA-067.0 > MFI-500.0. For clarity, the remaining ASA and MFI samples are omitted from this figure, but their behaviors are



Fig. 9 Deactivation profiles observed over various solid acids with time on stream. a) Comparison of catalyst stability in (\Box) MFI-500.0, (\triangle) ASA-067.6, and (\bigcirc) ASA-005.3a. b) Comparison of catalyst stability in (x) PWA/SiO₂, (\bigcirc) ASA-005.3a, and (\bigtriangledown) γ -Al₂O₃.

Table 3 Summary of first order deactivation constants and relevant physicochemical properties

| Catalyst | BET surface area $(m^2 g^{-1})$ | Micropore area $(m^2 g^{-1})$ | Acid site density (µmol m^{-2}) | Average pore diameter (Å) | $k_{\rm d}~({\rm h}^{-1})$ |
|--|---------------------------------|-------------------------------|------------------------------------|---------------------------|----------------------------|
| ASA-005.3a | 610 | 0 | 0.55 | 42 | 0.4 |
| ASA-067.6 | 550 | 130 | 0.09 | 32 | 1.5 |
| MFI-500.0 | 360 | 101 | 0.11 | 5.3 | 5.2 |
| γ -Al ₂ O ₃ | 230 | 5 | 0.13 | 60 | 0.03 |
| PWA/SiO ₂ | 470 | 1 | 0.06 | 56 | 0.5 |

qualitatively captured by the illustrated data. Specifically, with the exception of ASA-067.0 (illustrated in Fig. 9a), all ASA samples displayed an activity profile comparable to ASA-005.3a (illustrated in Fig. 9a). The activity of all MFI samples decayed rapidly, and none differed significantly from the behavior of MFI-500.0 (illustrated in Fig. 9a). Analyzing the physical and chemical properties of this aluminosilicate series, we conclude that the stability of materials having comparable deprotonation energies correlates most strongly with microporosity and average pore diameter. Most ASA samples tested here had pore diameters on the order of 40-60 Å, and they displayed similar stability when placed on stream, whereas ASA-067.0 - the least stable of the ASA series - had a relatively large micropore area (130 m² g⁻¹) and smaller pores on average (33 Å). This conclusion is further evidenced by the fact that MFI-500.0, with a higher micropore fraction and a smaller average pore diameter (5.3 Å), deactivates the most rapidly of any material considered. Since ASA-005.3a has both a higher areal acid site density and better stability than ASA-067.0 (Table 3), it appears that increasing acid site proximity does not promote coke deposition during GVL decarboxylation. Finally, since multiple ASA samples of varying Brønsted: Lewis site ratios display comparable deactivation profiles, we suggest that Lewis acidity does not promote coke formation during GVL decarboxylation. The results summarized to this point suggest that mesoporous aluminosilicates with low Si: Al ratios (high acid site densities) should offer the best compromise of activity and stability during GVL decarboxylation. Since increasing acid site proximity does not appear to diminish stability during GVL decarboxylation, high Brønsted site densities in mesoporous aluminosilicates can offset their reduced intrinsic activity compared to microporous zeolites (e.g., MFI).

Although not as dramatic an effect as changing pore dimensions, variation in the chemical nature of the acid site can also lead to changes in stability (Fig. 9b). Deactivation constants for this series range from 0.03 h⁻¹ for the most stable material, γ -Al₂O₃, to roughly 0.5 h⁻¹ for the least stable material, 5% PWA/SiO₂. Assuming that pore dimensions in each of these materials are sufficiently close to not alter deactivation kinetics (40–60 Å), we conclude that materials with relatively low deprotonation energies (*e.g.*, PWA/SiO₂, 1050– 1100 kJ mol⁻¹) are less stable than those with relatively high deprotonation energies (*e.g.*, ASA, ≈1200 kJ mol⁻¹), implying that facile deprotonation of Brønsted sites exacerbates coke formation during GVL decarboxylation. Lewis sites in γ -Al₂O₃ appear to be more stable than analogous Brønsted sites in ASA. Observed decarboxylation barriers are relatively high over γ -Al₂O₃ (172 kJ mol⁻¹), which implies lower reaction rates and higher operating temperatures; however, stable on-stream performance and unique selectivity to LAOs make γ -Al₂O₃ an intriguing catalyst for GVL decarboxylation.²¹

Conclusions

Rates of GVL decarboxylation in anhydrous environments correlate most strongly with the Brønsted acidity of the catalyst, and we have observed invariant turnover frequencies over Brønsted sites in both ASA and MFI over a range of Si: Al and Brønsted: Lewis ratios. Lewis sites associated with extraframework aluminum appear less active than Brønsted sites, and they do not contribute significantly to total decarboxylation rates in aluminosilicates. GVL decarboxylation barriers scale with the deprotonation energy of a Brønsted site; however, sites with low apparent barriers are not necessarily more intrinsically active than those with high apparent barriers. For example, supported PWA is less active than crystalline and amorphous aluminosilicates despite having a substantially lower apparent activation barrier. Additionally, even though Brønsted sites in MFI and ASA have similar deprotonation energies and experimentally observed decarboxylation barriers, the two aluminosilicates display substantially different turnover frequencies. The above observations may suggest that the local structure of a Brønsted site is important in defining its intrinsic decarboxylation activity; however, a limited microkinetic description of GVL decarboxylation and uncertainty in turnover frequency determination prevent rigorous support of this conclusion.

Based on the materials considered, aluminosilicates look to be the most practical for GVL decarboxylation under working conditions. Within this class of catalysts, pore diameter appears to be one of the most critical design parameters, influencing both activity and stability. Specifically, Brønsted sites in microporous MFI are more active than those in mesoporous ASA; however, GVL diffusion is hindered in MFI, leading to transport limitations at high temperatures. Furthermore, the loss of activity in microporous samples due to coke formation is more severe than in mesoporous analogs. Coke deposition seems to be associated with Brønsted acidity, but it does not scale with Brønsted site proximity. This suggests that catalysts with high acid site densities can be realistically employed for GVL decarboxylation. As a final recommendation, we propose that well-defined, mesoporous aluminosilicates (e.g., Al-MCM41) with low Si: Al ratios may offer the best compromise of activity and stability in GVL decarboxylation.

Abbreviations

- GVL γ -valerolactone
- PWA phosphotungstic acid
- ASA amorphous silica alumina
- DC decarboxylation
- PEA pentenoic acid
- DPE deprotonation energy
- LAO linear alpha olefin
- TOF turnover frequency
- TPD temperature programmed desorption
- IPA isopropylamine

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