

Mechanism and Kinetics of Ethanol–Acetaldehyde Conversion to 1,3-Butadiene over Isolated Lewis Acid La Sites in Silanol Nests in Dealuminated Beta Zeolite

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(AcH) conversion to 1,3-butadiene (1,3-BD) is an alternative process for 1,3-BD production. The present investigation reports the preparation and characterization of isolated La sites introduced into the silanol nests in DeAlBEA as well as detailed studies of the mechanism and kinetics for the conversion of an EtOH–AcH mixture to 1,3-BD. La sites supported on DeAlBEA are found to be present as (\equiv SiO)₂La–OH groups that are H-bonded with adjacent Si–OH groups, possessing high C–C coupling activity and stability, superior to state-of-the-art Y-DeAlBEA. La sites supported on silica (La-SiO₂) with a similar chemical structure but no H-bonding interaction with Si–OH groups were prepared for comparison. Lewis acid La sites promote AcH aldol condensation, and the activity of



such sites is nearly identical for both La-DeAlBEA and La-SiO₂. The rate of C₄ product formation increases by a factor of 4.8 upon addition of EtOH to the feed of AcH over La-DeAlBEA, whereas that over La/SiO₂ remains unchanged. Investigation of the mechanism and kinetics of AcH aldol condensation and EtOH-AcH conversion to 1,3-BD revealed two C-C bond forming pathways—AcH aldol condensation by Lewis acid La sites and direct coupling of EtOH-AcH over H-bonded (\equiv SiO)₂La-OH···· HO-Si \equiv sites. This study provides important information about the role of the local environment of isolated Lewis acid sites and their effects on the direct coupling of EtOH and AcH to form 1,3-BD.

KEYWORDS: isolated La sites, ethanol-acetaldehyde conversion to 1,3-butadiene, C-C coupling, hydrogen-bonding interaction, reaction mechanism, kinetics

■ INTRODUCTION

1,3-Butadiene (1,3-BD) is a monomer for synthetic rubbers and other polymers.^{1–3} Today, about 95% of the global 1,3-BD is derived as a side product of the naphtha steam cracking process, in which ethene is the main product.^{4,5} However, due to the shift from naphtha cracking to direct dehydrogenation of light alkanes (from shale gas) to produce ethene and propene, the supply of 1,3-BD is increasingly threatened.⁶ For this reason, the conversion of ethanol to butadiene (ETB) using bioethanol has received considerable recent attention.^{1,3,7–11} The rapid commercialization of coal to ethanol (EtOH) in China has also motivated interest in EtOH upgrading processes.^{12,13}

The production of 1,3-BD from EtOH was first reported in the 1900s via two routes—the one-step (Lebedev) and the two-step (Ostromisslensky) processes, both of which were commercialized.⁷ Both ETB processes are proposed to proceed by similar reaction pathways: (i) EtOH dehydrogenation to acetaldehyde (AcH); (ii) aldol condensation of AcH to produce acetaldol; (iii) rapid acetaldol dehydration to form crotonaldehyde; (iv) Meerwein–Ponndorf–Verley (MPV) reduction of crotonaldehyde with EtOH to generate equal amounts of crotyl alcohol and AcH, which can participate in step (ii); and (v) crotyl alcohol dehydration to produce 1,3-BD.^{9,14} Within this complex network, the formation of C–C bonds between C_2 reactants (AcH and EtOH) is the critical step for the generation of 1,3-BD.

Research during the last two decades has shown that the mechanism of C–C bond formation depends critically on the

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composition and structure of the catalytically active centers.^{1,3,15–19} Silica-supported transition metal Lewis acids and magnesia-silica mixed oxide catalysts have been reported to be active for C-C bond formation, with the former class of catalysts exhibiting higher activity.^{1,7} Considerable attention has been devoted recently to investigating various transition metal cations as catalysts for the ETB reaction.^{7,20–25} Supported Zr,^{26,27} Nb,^{28,29} Hf,²⁵ Ta,³⁰ and La³¹ exhibit good activity for C-C coupling and are regarded as active centers for the EtOH-AcH conversion to 1,3-BD. The composition of the support to which Lewis acid sites are grafted also plays an important role in ETB catalysis. The C-C coupling activity of Lewis acid sites can be enhanced remarkably when the support is changed from amorphous silica to siliceous zeolites.^{3,7,15,31,32} Under similar reaction conditions, Ag/ZrO₂ supported on dealuminated Beta (DeAlBEA) zeolite is four times more active than Ag/ZrO₂/SiO₂.³³ We have recently reported that the rate of 1,3-BD formation at 573 K was about 70 times higher when isolated Lewis acid Y sites were incorporated into the silanol nests of DeAlBEA zeolite, compared with Y supported on amorphous silica.³ The superior activity of Y/ DeAlBEA was ascribed to hydrogen (H)-bonding between the -OH group of $(\equiv SiO)_2Y$ -OH and adjacent $\equiv Si$ -OH present in silanol nests of DeAlBEA. Such interactions are not present when Y is supported on silica. A similar promoting effect was also found for acetone condensation to isobutene over grafted Hf sites with and without H-bonding interaction between adjacent silanol groups.³⁴ Active sites having the structure of $(\equiv$ SiO)₃Hf-OH···HO-Si \equiv were 4.5 times more active for C–C coupling compared to $(\equiv SiO)_3Hf$ –OH. More recently, Zhang et al. have also found that C-C coupling occurs more rapidly over Lewis acid Y sites incorporated into DeAlBEA compared with Y supported on silica and deboronated MWW; the higher activity of the former catalyst was ascribed to the higher density of Lewis acidic Y sites.³

While the importance of Lewis acid catalysts for C-C coupling has been recognized, the intrinsic role of the local structure of active sites and the influence of support materials on its performance remain unclear. To date, the only consensus is that tri-, quadra-, and pentavalent metals, e.g., $Y_{,3}^{,3}$ La,³¹ Zr,^{26,27} Hf,²⁵ Nb,^{28,29} and Ta,³⁰ present in open ((Si-O-Mⁿ⁺)_{n-1}-OH) sites are generally more active for C-C coupling than closed $((Si-O-M^{n+})_n)$ sites.^{18,24,35-38} The mechanistic recognition of the influence of interactions between open-structure Lewis acid sites and characteristic groups of supports (Si-OH groups) has rarely been reported. To this point, trivalent metals such as Y/La/Ce are of particular interest because of their very high C-C coupling activity once they are introduced into zeolite silanol nests. However, development of a fundamental understanding of the structure-performance relationship for the Y/La/Ce-catalyzed ETB process has been hindered by the absence of knowledge about the interactions of Lewis acid centers with their environment and difficulties in relating this information to the ETB reaction network.^{14,17,18,39,40} Prior investigation of the Lewis acid-catalyzed ETB process has generally considered AcH aldol condensation to be the key step in C-C bond formation; however, serious catalyst deactivation made it difficult to investigate the reaction mechanism and kinetics.

In the work reported here, we have developed a comprehensive understanding of the reaction mechanism and kinetics for the formation of 1,3-BD via aldol condensation of AcH and by condensation of AcH and EtOH. Lewis acid La

exhibited high C-C coupling activity, and because this activity was stable, it enabled the measurement of the kinetics of 1,3-BD formation via both processes. The structure of isolated La introduced into the silanol nest of DeAlBEA was established to be $(\equiv SiO)_2La - OH \cdots HO - Si \equiv$, which was confirmed using infrared spectroscopy of hydroxyl groups and adsorbed pyridine, deuterated acetonitrile, and 2,6-di-tert-butylpyridine, and X-ray absorption spectroscopy (XAS). To clarify the intrinsic influence of the support silanol groups, La was grafted onto silica for comparison. This catalyst exhibited lower activity for EtOH-AcH conversion to 1,3-BD compared to La-DeAlBEA. Silica-supported La sites were formed with a structure of $(\equiv SiO)_2La - OH$ but with no evidence for Hbonding of this species with neighboring silanol groups. The two types of isolated La sites exhibited almost identical aldol condensation activity, indicating the presence of H-bonding interaction-assisted new C-C bond formation mechanisms over La-DeAlBEA. The mechanism and kinetics of C-C bond formation were investigated over (≡SiO)₂La-OH…HO-Si \equiv . It was found that the kinetics of C-C bond formation depended on the local environment of the La site. Two distinct C-C bond formation pathways were identified—AcH aldol condensation over Lewis acid La centers and direct coupling of EtOH and AcH over H-bonded (\equiv SiO)₂La-OH···HO-Si \equiv centers, the kinetics of the latter pathway being elucidated in the present study for the first time.

RESULTS AND DISCUSSION

Catalyst Characterization. The generation of silanol nests upon dealumination was evidenced by IR spectra of surface hydroxyl groups and adsorbed pyridine for H-BEA and DeAlBEA. The IR spectrum of H-BEA presented in Figure S1A exhibits a sharp band at 3743 cm⁻¹ corresponding to isolated silanol (Si-OH) groups, a band at 3606 cm⁻¹ corresponding to the stretching vibration of Brønsted acid Al-OH groups, and two bands at 3660 and 3780 cm⁻¹ corresponding to hydroxyl groups associated with extraframework Al species. 41-43 After dealumination, all Al-related IR bands disappear, accompanied by the appearance of a broad band centered at around 3520 cm⁻¹ attributed to silanol nests in which the \equiv Si-OH groups are H-bonded.⁴⁴ It is also observed that the center of the IR band for isolated silanol groups shifts to 3732 cm⁻¹, likely due to the generation of internal silanol groups.⁴² Figure S1B presents IR spectra of pyridine adsorbed on H-BEA and DeAlBEA. For DeAlBEA, all these IR bands for pyridine interacting with Brønsted and Lewis acid sites (1637, 1545, 1490, 1620, and 1453 cm⁻¹) are absent, and instead, two intense bands appear at 1592 and 1445 cm⁻¹ due to adsorption of pyridine on H-bonded silanol nests.^{3,31,34,45} These changes suggest that silanol nests are created upon dealumination.

La was introduced into DeAlBEA zeolite by wet impregnation. ICP-OES analysis (Figure S2) shows the near quantitative introduction of La, confirming the effectiveness of the strategy used to incorporate La into DeAlBEA. XRD patterns of La-supported dealuminated Beta samples (Figure S3) exhibit identical characteristic peaks of BEA, indicating preservation of the zeolite framework upon La incorporation.^{3,41,42,44} No diffraction peaks for bulk La₂O₃ are observable for materials with a La/Al ratio up to 0.60, suggesting a high dispersion of La species and the absence of XRD-detectable metal oxide nanoparticles. To identify the detailed dispersion of La sites supported over DeAlBEA, atomic-resolution Cs-corrected HAADF-STEM measurements were conducted for 0.12La-DeAlBEA. Figure 1A,B clearly



Figure 1. (A,B) Atomic-resolution Cs-corrected, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images (white dots representing La atoms are outlined by yellow dashed circles) and (C) energy-dispersive X-ray mappings of 0.12La-DeAlBEA.

shows evidence for isolated La atoms and no evidence for small clusters of LaOx species, suggesting that La is atomically dispersed. Figure 1B shows lattice fringes with consistent orientations over the entire zeolite crystal. Additionally, energy-dispersive X-ray (EDX) spectral mappings further reveal that the La atoms are highly and homogeneously dispersed throughout the BEA zeolite crystal (Figure 1C).

Changes in surface hydroxyl groups were observed upon the introduction of La into DeAlBEA. As shown in Figure 2A, the intensities of broad IR bands centered at around 3520 cm⁻¹ decrease significantly, indicating that La is grafted into the silanol nests of DeAlBEA likely via the formation of Si-O-La linkages.⁴² Moreover, the observed attenuation of the IR band at around 3732 cm⁻¹ indicates that internal silanol groups are also involved in the grafting of the La species. IR spectra of adsorbed pyridine were acquired to explore the acid properties of La-DeAlBEA. Consistent with previous studies for metal-substituted zeolite materials,^{32,46} La-DeAlBEA exhibits IR bands for pyridine interacting primarily with Lewis acid centers as evidenced in Figure 2B by the appearance of a band at 1599 cm⁻¹. A significant decrease in the intensity of the signal for Hbonded pyridine at 1592 cm⁻¹ is also observed, which is attributed to the consumption of silanol nests during the grafting of La.²⁰ Because of band overlap, the IR band in the region of 1440–1460 cm⁻¹ associated with pyridine adsorption on Lewis acid sites (the ω_{19b} vibrational mode) cannot be distinguished from the IR band of pyridine interacting via Hbonding with the silanol group in silanol nests (1445 cm⁻¹).⁴⁷ The absence of bands at 1545 or 1637 cm⁻¹ indicates the absence of Brønsted acid sites that are strong enough to protonate pyridine.³ Therefore, the IR band at 1490 cm⁻¹ is predominantly attributed to pyridine adsorbed on the Lewis acid La sites. Since the integrated intensity of the band at 1490 cm⁻¹ increases linearly with increasing La/Al ratio up to 0.24 (Figure S4A), it is reasonable to conclude that La sites on La-DeAlBEA for La/Al < 0.24 are present as isolated sites. Consistent with this interpretation, the areas of IR bands for pyridine adsorption on Lewis acid sites, obtained by deconvolution from the overlapping peaks at 1560-1600 cm⁻¹, also exhibit a nearly linear dependence on the La/Al ratio up to a value of 0.24 (Figure S4B).

IR spectroscopy of adsorbed perdeuterated acetonitrile (CD₃CN) was further applied to distinguish Lewis acid sites

from silanol groups.⁴⁸ IR spectra of CD₃CN adsorbed on DeAlBEA and 0.06La-DeAlBEA taken as a function of He purging time are illustrated in Figure S5. DeAlBEA exhibits a peak at 2273 cm⁻¹, a characteristic of the ν (C \equiv N) stretching vibration of CD₃CN interreacting with H-bonded silanol groups (silanol nests).⁴⁸⁻⁵⁰ For 0.06La-DeAlBEA, the center of the IR band shifts to 2287 cm⁻¹ attributable to CD₃CN adsorbed on Lewis acidic sites and is accompanied by the appearance of a shoulder peak at 2273 cm⁻¹ for CD_3CN adsorption on residual silanol nests.^{39,51,52} With increasing purge time, the peak intensity decreases due to a gradual decrease in CD₃CN coverage but finally remains nearly constant after purging for 40 min. Quantitative analysis of Lewis acid sites was, therefore, based on the IR spectrum recorded at 50 min. Figure 2C presents IR spectra acquired for CD₃CN adsorbed on DeAlBEA and La-DeAlBEA with La/Al ratios ranging from 0.06 to 0.60. For better quantification of the integrated area of the band at 2287 cm⁻¹, peak deconvolution utilizing a fixed band center and fwhm was used to exclude the contribution from the overlapping band at 2273 cm⁻¹ due to CD₃CN adsorbed on silanol nests. The area of the IR band for Lewis acid La sites shows a linear increase up to La/Al = 0.24 and then increases at a much lower rate for higher values of La/Al (Figure 2D). This suggests that isolated Lewis acid La sites predominate for catalysts with La/Al < 0.24, while lanthanum oxide clusters may be generated at higher La loadings.

2,6-Di-tert-butylpyridine (DTBPy) is able to distinguish weak Brønsted acidity arising from H-bonding interaction among M-OH groups of open Lewis acid sites and adjacent silanol groups from siliceous zeolitic supports (i.e., M-OH… O(H)-Si).7,48,53,54 Previous studies have shown that all Brønsted acid sites in BEA zeolite can be accessed by DTBPy.^{39,55} Figure 2E presents the IR spectra of DTBPy adsorbed on La-DeAlBEA. Bands at 3359, 1612, and 1531 cm⁻¹ for vibrations of protonated DTBPy⁵⁵ are clearly observed for all samples of La-DeAlBEA, and their intensity increases with the increasing La loadings. The observed changes can be attributed to DTBPy adsorption on H-bonded La–OH and Si–OH groups. The band at 3359 cm⁻¹ for ν (N– H⁺) vibrations is used to quantify the content of weak Brønsted acid sites.⁵⁶ As seen in Figure 2F, the integrated intensity increases linearly as the La/Al ratio increases to 0.24, suggesting that isolated La sites with a La-OH group (most likely presented as an open chemical structure, i.e., La sites are grafted onto two Si-O-La bonds and one hydroxyl (-OH) group) are mainly formed via grafting onto the zeolitic framework.

The acid properties of La sites grafted onto SiO₂ (0.85 wt % La-SiO₂) and DeAlBEA (0.06La-DeAlBEA) supports, which have nearly identical La loadings, were comparatively investigated. Figure S6 presents the IR spectra of pyridine adsorbed on 0.06La-DeAlBEA and 0.85 wt %La-SiO₂ recorded after purging 5 to 25 min. Introduction of pyridine leads to the appearance of Lewis acid IR bands at around 1598 and 1445 cm⁻¹ over both catalysts. We further note that the intensity of the IR spectra remains almost unchanged after purging for 25 min. The IR spectra for pyridine adsorbed on 0.06La-DeAlBEA and 0.85 wt %La-SiO₂ recorded at 25 min are compared in Figure 3A. As shown, the intensity of the IR bands for pyridine adsorption on 0.06La-DeAlBEA. As discussed above, the IR bands at about 1598 and 1445 cm⁻¹



Figure 2. (A) Effect of La loadings on the FTIR spectra of the surface hydroxyl groups on DeAlBEA and La-DeAlBEA. FTIR spectra of adsorbed (B) pyridine, (C) CD_3CN , and (E) DTBPy for DeAlBEA and La-DeAlBEA. Plots of the integrated area for (D) CD_3CN adsorption band at 2287 cm⁻¹ and (F) DTBPy adsorption band at 3359 cm⁻¹ versus La/Al ratio for La-DeAlBEA.

for 0.06La-DeAlBEA contain contributions from pyridine interacting with both Lewis acid La sites and residual Hbonded silanol nests. To distinguish the contribution of Lewis acid La sites over each catalyst, the IR band centered at 1598 cm⁻¹ was deconvoluted (Figure 3C,D). The integrated intensity of the band for pyridine adsorption on Lewis acid La sites on 0.06La-DeAlBEA and 0.85 wt %La-SiO₂ is nearly identical (1.1 vs 0.9), suggesting the similarly high dispersion of Lewis acid La sites on both DeAlBEA and SiO₂. To further clarify the local environment of Lewis acid La sites over both supports, we also employed IR spectroscopy of adsorbed DTBPy (Figure 3B). In sharp contrast to what is observed on 0.06La-DeAlBEA, the IR bands for protonated DTBPy are nearly undetectable over SiO₂ and 0.85 wt %La-SiO₂. The significantly weaker IR bands observed for 0.85 wt %La-SiO₂ compared to 0.06La-DeAlBEA indicate the absence of H-bonding interaction between La–OH and Si–OH groups over SiO₂.

¹H MAS NMR spectroscopy was used to further characterize the changes of hydroxyl groups over DeAlBEA and Lasupported DeAlBEA with La/Al ratios of 0.12 and 0.24. Spectral peak deconvolution was conducted to distinguish the overlapping peaks. As shown in Figure S7, after deconvolution, six similar peaks can be identified for all three samples, and the estimated concentration of each –OH group is summarized in Table S1. ¹H MAS NMR of DeAlBEA shows signals at 1.0, 1.7, 2.0, 2.3, 3.1, and 4.5 ppm. The peak at 1.7 ppm and the very small peak at 1.0 ppm are assigned to isolated silanol groups.⁵⁷



Figure 3. (A) FTIR spectra of pyridine adsorbed on 0.06La-DeAlBEA and 0.85 wt %La-SiO₂. (B) FTIR spectra of DTBPy adsorbed on SiO₂, 0.85 wt %La-SiO₂, DeAlBEA, and 0.06La-DeAlBEA. Deconvolution of the IR spectra for pyridine adsorbed on (C) 0.06La-DeAlBEA and (D) 0.85 wt % La-SiO₂.



Figure 4. (A) Normalized La K-edge X-ray absorption near-edge spectra (XANES) of 0.06La-DeAlBEA and 0.85 wt % La-SiO₂ catalysts as well as La standard under ambient conditions. (B) Fourier-transformed k^2 -weighted extended X-ray absorption fine structure spectra (EXAFS) of 0.06La-DeAlBEA and 0.85 wt % La-SiO₂ catalysts. Curve fitting of the real and imaginary components of the EXAFS data for (C) 0.06La-DeAlBEA and (D) 0.85 wt %La-SiO₂ catalysts. Catalysts were pretreated at 573 K in He for 30 min.

The peaks at 2.0 and 2.3 ppm are internal silanol groups, while the peak at 3.1 ppm represents H-bonded silanol nests.³⁴ The broad peak centered at 4.5 ppm is due to strongly H-bonded Si-OH groups and/or clusters of adsorbed H₂O.^{34,44} Introduction of La leads to an obvious loss of silanol nests and internal silanol groups characterized by the peaks at around 3.1, 2.0, and 2.3 ppm, while the peak attributable to isolated Si-OH groups remains almost unchanged (0.37-0.45 mmol/g). These observations indicate that La species are grafted onto the silanol nests and internal silanols in agreement with our IR observations. We note that the ¹H NMR signal for La-OH groups has been reported to be characterized by a proton chemical shift of around 2.5 ppm in the super cages of X and Y zeolites.⁵⁸ This feature is quite close to that of Hbonded internal Si-OH groups detected at 2.3 ppm. Consequently, the chemical shifts at 2.3 ppm for 0.12La-DeAlBEA and 0.24La-DeAlBEA could have contributions from both La-OH groups and residual internal Si-OH groups.

IR analysis of adsorbed pyridine, CD_3CN , and DTBPy on La-DeAlBEA as well as ¹H MAS NMR spectroscopy reveals the generation of isolated Lewis acid sites arising from La grafting into the silanol nest on DeAlBEA and the formation of weak Brønsted acid sites due to H-bonded La $-OH\cdots O(H)$ -Si structures. In sharp contrast, La sites grafted onto SiO₂ are predominantly present as isolated La sites with an open structure similar to that for La-DeAlBEA but no H-bonding interaction with proximal Si-OH groups.

The oxidation state and coordination geometry of La sites were investigated by using XAS. XANES spectra for La₂O₃, 0.85 wt % La-SiO₂, and 0.06La-DeAlBEA are presented in Figure 4A. The XANES spectrum of 0.06La-DeAlBEA is similar to that of La₂O₃, indicating that La in the La-DeAlBEA sample is best described as La(III). The EXAFS spectra of La₂O₃, 0.85 wt % La-SiO₂, and 0.06La-DeAlBEA are displayed in Figure 4B. Fitting of the real and imaginary components of the Fourier transform of the EXAFS data yields the coordination number and bond distance given in Table 1.

Table 1. Fitted Parameters for Fourier-Transformed La K-Edge EXAFS of La-DeAlBEA and La-SiO $_2$

catalyst	path	N_{i}	$R_{\rm i}$ (Å)	$\sigma_{\rm i}^2 \times 10^{-3}$
0.06La-DeAlBEA	La-O	3	2.44 ± 0.02	6.0 ± 2.2
	La-O	4	2.62 ± 0.02	6.0 ± 2.2
	La–(O)–Si	3	4.01 ± 0.03	9.7 ± 5.3
0.85 wt % La-SiO $_2$	La-O	3	2.43 ± 0.02	2.8 ± 1.2
	La-O	3	2.60 ± 0.02	2.8 ± 1.2
	La–(O)–Si	2	4.00 ± 0.05	9.3 ± 4.6

The multielectron excitation (MEE) removal process of all spectra was applied to eliminate the influence of strong multielectron excitations of La. The changes in k-space and R-space data before and after MEE removal are shown in Figures S8 and S9. Compared to the spectrum of La₂O₃, only one strong peak was observed in the spectra of 0.85 wt % La-SiO₂ and 0.06La-DeAlBEA. The absence of La–La⁵⁹ and La–O–La⁶⁰ backscattering in the second shell of the spectra of 0.06La-DeAlBEA and 0.85 wt % La-SiO₂ indicates that the La atoms are isolated. The results of fitting shown in Figure 4C suggest that there are two La–O scattering paths with distances of about 2.44 and 2.62 Å. The first peak is attributed to the La–O bond formed upon condensation of La with two silanol groups and one La–OH group having a CN_{La–O} ~ 3,

and the second peak is attributed to one dative bond with the silanol group in DeAlBEA and interaction with three molecules of H_2O with a total $CN_{La=O}$ of ~4.⁶¹⁻⁶³ The two coordination distances are consistent with La-containing compounds; for example, the La–O bond in La_2O_3 is in the range of 2.41–2.50 $Å^{64}$, while the La–O bond distance in the aqueous $La(H_2O)_9^{3+}$ is ca. 2.60 Å.⁶⁵ The two bond lengths found in the best curve fitting results, together with the DTBPyadsorbed IR results, also indicate the presence of the La-OH group. Hence, La is proposed to be present as \equiv Si-O- $La(OH)-O-Si \equiv$, with La also datively coordinated with one ≡Si-OH group and three water molecules. XAS analysis of 0.85 wt %La-SiO₂ was also carried out, and the corresponding XANES spectrum and EXAFS pattern are shown in Figure 4A,B, and the fitted EXAFS data are shown in Figure 4D, whereas fitted parameters are listed in Table 1. The curve fitting results for 0.85 wt %La-SiO₂ suggest that there are 3 La-O bonds corresponding to La attached to two O atoms in the silica support and one La-OH group and another 3 bonds tentatively assigned to $La-(OH_2)$.

In summary, based on the information obtained from IR spectroscopy as well as XAS analysis of La-DeAlBEA and La-SiO₂, it is possible to propose the chemical structure of isolated La sites supported on DeAlBEA and SiO₂. As shown in Scheme 1, La in La-DeAlBEA is predominantly bonded to two





O atoms of the support, one –OH group, and datively coordinated with one adjacent Si–OH group. The weak Brønsted acidity of La-DeAlBEA detected by DTBPy IR spectroscopy and the existence of strongly H-bonded silanol nests over DeAlBEA support the proposal that La–OH exhibits H-bonding interactions with Si–OH groups on DeAlBEA. In contrast to DeAlBEA, SiO₂ mainly possesses isolated silanol groups³⁴ and no Brønsted acidity is evidenced by DTBPy IR spectroscopy for La-SiO₂. Consequently, H-bonding interactions between La–OH groups and Si–OH groups do not appear for La supported on SiO₂.

Ethanol Conversion over DeAlBEA and La-DeAlBEA. The conversions of EtOH at 603 K over DeAlBEA and La-DeAlBEA are shown in Figure 5 as a function of time-onstream (TOS). The principal process occurring over DeAlBEA is dehydration of EtOH to produce ethene and diethyl ether (DEE), which occurs with a total selectivity of about 99.7%.^{3,21} For 0.12La-DeAlBEA, ethene and DEE remain the principal products together with a small amount of AcH (<2%). This suggests that Lewis acid La sites are nearly inactive for EtOH dehydrogenation.^{3,21} Note that the initial rate of EtOH dehydration over DeAlBEA is higher than that over 0.12La-



Figure 5. EtOH conversion and product distribution catalyzed by (A) DeAlBEA and (B) 0.12La-DeAlBEA as a function of TOS. (C) Comparison of the initial rate of EtOH dehydration over DeAlBEA and 0.12La-DeAlBEA. Reaction conditions: $m_{cat} = 20$ mg, T = 603 K, $F_{He} = 20$ mL/min, and $p_{EtOH} = 5.34$ kPa.



Figure 6. (A) Conversions of EtOH and AcH and (B) product distribution for EtOH–AcH conversion over 0.12La-DeAlBEA as a function of TOS. Reaction conditions: $m_{cat} = 10 \text{ mg}$, T = 603 K, $F_{EtOH-AcH} = 0.189 \text{ mL/h}$, $m_{EtOH}/m_{AcH} = 6$, $P_{EtOH} = 2.73 \text{ kPa}$, $P_{AcH} = 0.48 \text{ kPa}$, and total flow rate = 41.2 mL/min.



Figure 7. (A) Effect of AcH partial pressure on the conversions of the EtOH–AcH mixture and product distribution at TOS = 5 min. (B) Selectivity of 1,3-BD and (C) rate of 1,3-BD formation over 0.12La-DeAlBEA as functions of AcH partial pressure and TOS. Reaction conditions: $m_{cat} = 10 \text{ mg}$, 623 K, $P_{EtOH} = 2.73 \text{ kPa}$, $P_{AcH} = 0.32$, 0.48, 0.71, and 0.95 kPa, and total flow rate = 41.2 mL/min.

DeAlBEA (Figure 5C), a consequence of the stronger acidity of silanol nests in comparison to Lewis acid La sites for catalyzing EtOH dehydration. It is also observed that the EtOH conversion over DeAlBEA remains relatively stable for 150 min, whereas that over 0.12La-DeAlBEA decreases monotonically with TOS due to gradual poisoning of the sites active for dehydration by the AcH produced, as was observed for Y-DeAlBEA.^{3,66} Li, Dai, and co-workers have investigated the mechanism of catalyst deactivation during EtOH conversion to 1,3-BD.⁶⁶ They found that acetaldol formed by AcH aldol condensation can proceed via dehydrogenation to produce 3-oxobutanal, which then reacts with water to produce acetone. Through a cascade of AcH and acetone self- and cross-condensation, long-chain unsaturated aldehydes/ketones are formed that further convert to 2,4dimethyl benzaldehyde via cyclization. These processes gradually lead to the coverage of the active sites and catalyst deactivation.

As can be seen in Figure 5B, almost no 1,3-BD is generated during the reaction of pure EtOH over 0.12La-DeAlBEA, suggesting that AcH is a necessary precursor for C–C bond formation in the ETB process. This reaction was investigated



Figure 8. Initial formation rates of 1,3-BD from EtOH–AcH conversion, measured at 2.73 kPa EtOH and 0.32 kPa AcH and 573 K, as a function of the La/Al ratio. (A) Rates normalized per catalyst mass. (B) Rates normalized per mole of La. The turnover frequency (TOF) rates of 1,3-BD formation for La-DeAlBEA with varying La contents are tested based on an identical space velocity relative to the La amount.



Figure 9. (A) Transient formation rates of crotonaldehyde from AcH conversion over 0.06La-DeAlBEA during the introduction and removal of pyridine. Without EtOH, crotonaldehyde is produced with a selectivity above 95%. After introducing EtOH, 1,3-BD is formed with a selectivity of about 65%. (B) Transient formation rates of C₄ products over 0.06La-DeAlBEA during introduction and removal of EtOH. Reaction conditions: 573 K, $m_{cat} = 10 \text{ mg}$, $p_{AcH} = 0.41 \text{ kPa}$, and total flow rate = 40.5 mL/min.

by feeding 0.48 kPa of AcH together with EtOH (2.73 kPa); Figure 6 shows the conversion of an EtOH–AcH mixture (A) and the distribution of products formed (B) at 603 K. 1,3-BD is observed immediately after TOS = 5 min with a high initial selectivity of ~66.0% at an EtOH conversion of 17.8% and an AcH conversion of 56.2%, indicating that isolated La sites are catalytically active for the C-C coupling process.³ Moreover, as the reaction proceeds, the selectivity to 1,3-BD increases to 68.8% within the initial 20 min and then reaches a plateau of about 70% for longer TOS; concurrently, the selectivity to ethene decreases monotonically. As noted earlier, this trend is attributed to the inhibition of EtOH dehydration caused by gradual AcH poisoning of the remaining silanol nests. Figure 6B shows that other C4 products are also observed in small proportions, most notably butenes, crotyl alcohol, and crotonaldehyde, with a total selectivity below 15%.^{3,10,15,17,21}

The reaction of EtOH and AcH was further investigated as a function of the feed AcH partial pressure for a constant feed EtOH partial pressure of 2.73 kPa, as shown in Figure 7. The conversion of EtOH within the range of AcH partial pressures explored changes from 15.6% at a high AcH partial pressure to 17.0% at a low AcH partial pressure. As the AcH partial pressure increases from 0.32 to 0.95 kPa, the selectivity toward dehydration products, mainly ethene, decreases significantly and the initial selectivity to 1,3-BD increases from 47.4 to

71.3%. Moreover, as shown in Figure 7B, the induction period for obtaining a stable 1,3-BD selectivity remarkably shortens at higher AcH partial pressures. Figure 7C illustrates the rate of 1,3-BD formation as a function of AcH partial pressure and TOS. The introduction of AcH enhances the formation of 1,3-BD significantly. All these observations point to AcH inhibition of EtOH dehydration and promotion of C-C coupling. However, we note that if the AcH partial pressure is too high, the catalyst stability is impaired due to the enhanced formation of oxygen- or nonoxygen-containing coke precursors.^{14,66} This result supports the hypothesis that deactivation occurs via a combination of self- and cross-condensation of AcH and acetone that produces long-chain unsaturated aldehydes/ ketones, which lead to the coverage of the active sites and their deactivation. It is noted, though, that the catalyst could be regenerated by calcination in air at 823 K.⁶⁶

To clarify the effect of the nature of La species on their activity for C–C coupling, initial rates of 1,3-BD formation at TOS = 5 min were measured at 573 K under differential reaction conditions using a feed containing 2.73 kPa EtOH and 0.32 kPa AcH as a function of the La/Al ratio. As observed in Figure 8A, the rate of 1,3-BD formation normalized per gram of catalyst increases linearly with La loading up to a La/Al ratio of 0.24 but then reaches a plateau for higher values. When the rate of 1,3-BD formation is normalized per atom of La (Figure 1,3-BD formation is normalized per atom of La (Figure 2,3-BD formation is normalized per atom of La (Figure 2,3-BD formation is normalized per atom of La (Figure 2,3-BD formation is normalized per atom of La (Figure 2,3-BD formation is normalized per atom of La (Figure 2,3-BD formation is normalized per atom of La (Figure 2,3-BD formation is normalized per atom of La (Figure 2,3-BD formation is normalized per atom of La (Figure 2,3-BD formation is normalized per atom of La (Figure 2,3-BD formation is normalized per atom of La (Figure 2,3-BD formation is normalized per atom of La (Figure 2,3-BD formation is normalized per atom of La (Figure 2,3-BD formation is normalized per atom of La (Figure 2,3-BD formation is normalized per atom of La (Figure 2,3-BD formation is normalized per atom of La (Figure 2,3-BD formation is normalized per atom of La (Figure 2,3-BD formation is normalized per atom of La (Figure 2,3-BD formation is normalized per atom of La (Figure 2,3-BD formation is normalized per atom of La (Figure 2,3-BD formation 2,3-BD

8B), the rate is nearly independent of the La/Al ratio for values from 0.06 to 0.24, suggesting that the active La sites are isolated. Previous studies support this conclusion, suggesting that isolated Lewis acid Ta,³⁸ Zr,⁴ and Y^{3,32} sites are the active centers for C–C bond formation. As the La/Al ratio increases from 0.24 to 0.60, the TOF rate of 1,3-BD formation decreases continuously, which may indicate the generation of less active LaO_x clusters or nanoparticles at higher La loadings. These experimental results agree well with the IR and XAS characterization results reported in Figures 2 and 4.

The specific roles of isolated Lewis acid La sites in the critical steps of the ETB process were explored further by decoupling the reaction network. The first step investigated was aldol condensation of AcH to crotonaldehyde, since this reaction is generally regarded as critical for the formation of C–C bonds in the ETB process, and it has been suggested that this step is catalyzed by isolated Lewis acid sites.^{15,17,18,67} However, investigation of the mechanism by which isolated Lewis acid-catalyzed AcH aldol condensation is still encumbered by rapid site deaction.¹⁵

As shown in Figure 9, pure AcH forms crotonaldehyde with a selectivity close to 100% and at a stable rate of about 0.009 mol/mol La/s over 0.06La-DeAlBEA under the reaction conditions chosen. Notably, acetaldol is not observed, indicating that the dehydration of acetaldol to produce crotonaldehyde is rapid. To elucidate the site requirements for AcH aldol condensation, pyridine was introduced continuously with the feed to titrate Lewis acid La sites. The rate of crotonaldehyde formation decreases rapidly from 0.009 to 0.004 mol/mol La/s upon the introduction of 0.12 kPa of pyridine but immediately returns back to 85% of the original rate when the flow of pyridine is terminated. This suggests that Lewis acidic La sites play a catalytic role in AcH aldol condensation.

In our earlier work on Y-DeAlBEA, it was proposed that addition of EtOH to AcH resulted in 1,3-BD formation via concerted EtOH-AcH coupling.³ To assess whether this pathway was also operative for La-containing catalysts, we compared feeding pure AcH and EtOH-AcH over 0.06La-DeAlBEA. Pure AcH was fed into the reactor first, then the feed was switched to an EtOH-AcH mixture while maintaining the same AcH partial pressure, and finally, the feed was switched back to pure AcH. As shown in Figure 9B, with pure AcH as the feed, crotonaldehyde forms at a stable rate of ~0.009 mol/mol La/s. When 2.73 kPa of EtOH is introduced into the AcH feed stream, the rate of C4 products (principally 1,3-BD) increases by a factor of 4.8 to 0.043 mol/ mol La/s. The C₄ product formation rate drops back to ~ 0.009 mol/mol La/s when the flow of EtOH is stopped. The reactant switching experiments clearly demonstrate the participation of EtOH in the generation of new C-C bonds, like what we observed over Y-DeAlBEA.³ Additionally, the rate of C_4 product formation over La-DeAlBEA is determined to be 0.035 mol/mol La/s with 2.7 kPa EtOH and 0.3 kPa AcH at 573 K based on the kinetics discussed below. This activity is slightly higher than that for Y-DeAlBEA under identical reaction conditions (0.0287 mol/mol Y/s).

It is notable that the conversion of AcH over 0.06La-DeAlBEA and 0.85 wt %La-SiO₂ for identical reaction conditions gives near-identical rates of crotonaldehyde formation (Figure S10), suggesting that Lewis acid La sites on 0.06La-DeAlBEA and 0.85 wt %La-SiO₂ are responsible for aldol condensation of AcH, despite the differences in the extent of local H-bonding local environment. As analyzed by pyridine adsorbed IR spectroscopy, the amounts of Lewis acid La sites over 0.06La-DeAlBEA and 0.85 wt %La are nearly identical. However, in the case of EtOH–AcH conversion, no significant enhancement in the C–C formation rate was observed compared with pure AcH conversion over 0.85 wt % La-SiO₂, suggesting that the Lewis acid center local environment, H-bonding interaction of La–OH with Si–OH groups of the zeolite framework, participates in the C–C bond formation under EtOH cofeeding conditions.

According to the traditional reaction mechanism for the ETB process, two molecules of AcH react to produce crotonaldehyde, which then reacts with EtOH to produce crotyl alcohol and AcH via the MPV reaction.^{4,14} The resulting crotyl alcohol then rapidly dehydrates to form 1,3-BD.⁷ To gain additional insights into the active sites responsible for each reaction step and to identify the rate-limiting step in the overall reaction, we investigated the reaction of AcH–EtOH, crotonaldehyde–EtOH, and crotyl alcohol over DeAlBEA and 0.06La-DeAlBEA, respectively. The rates of product formation in these studies are summarized in Table 2. Cofeeding 0.16

Table 2. Conversion of Intermediates over DeAlBEA and 0.06La-DeAlBEA a

		formation rate, mmol/g _{cat} /min			
catalyst	reactants	1,3-BD	butenes	crotyl alcohol	C ₄ products
0.06La- DeAlBEA	AcH-EtOH ^b	0.087	0.005	0.004	0.096
	crotonaldehyde- EtOH ^c	0.143	0.006	0.006	0.155
	crotyl alcohol ^d	0.096	0.002		0.098
	crotyl alcohol ^e	0.155	0.003		0.158
DeAlBEA	crotonaldehyde– EtOH ^c	0.015			0.015
	crotyl alcohol ^d	0.121	0.002		0.123

^{*a*}Reaction conditions: T = 573 K, $m_{cat} = 0.02$ g, and He flow rate = 40 mL/min. ^{*b*}AcH and EtOH reaction was measured with 0.32 kPa AcH and 2.73 kPa EtOH. ^{*c*}Conversion of crotonaldehyde and EtOH was measured with 0.16 kPa crotonaldehyde and 2.73 kPa EtOH. ^{*d*}Conversion of crotyl alcohol was measured with a crotyl alcohol partial pressure of 0.16 kPa. ^{*e*}Conversion of crotyl alcohol was measured with a crotyl alcohol partial pressure of 0.32 kPa.

kPa crotonaldehyde and 2.73 kPa EtOH at 573 K over 0.06La-DeAlBEA produces 1,3-BD at the rate of 0.143 mmol/ g_{cat} /min and total C₄ products (butenes and crotyl alcohol) at the rate of 0.155 mmol/ g_{cat} /min. These observations demonstrate almost complete conversion of crotonaldehyde, indicating that the MPV reaction between crotonaldehyde and EtOH proceeds rapidly for this catalyst under the reaction conditions investigated. By contrast, under similar conditions, only a negligible amount of 1,3-BD is produced over DeAlBEA. This observation suggests that the Lewis acid La sites are required to catalyze the MPV reaction, in line with the previous reports of Zn, Y, and La-containing catalysts.^{14,20}

When 0.16 or 0.32 kPa crotyl alcohol was fed to the reactor containing 0.06La-DeAlBEA, 1,3-BD was produced at the rate of 0.096 and 0.155 mmol/g_{cat}/min, respectively, suggesting that crotyl alcohol preferentially undergoes intramolecular dehydration, and this is a facile step in the process. Importantly, it is also noted that the rates of C₄ product formation via MPV and crotyl alcohol dehydration are both higher than that observed when AcH and EtOH are fed at a



Figure 10. (A) Dependence of aldol condensation rate on the partial pressure of AcH and temperature and (B) Arrhenius plot for AcH aldol condensation over 0.06La-DeAlBEA. Reaction conditions: 513-573 K, $m_{cat} = 10$ mg of 0.06La-DeAlBEA, and total flow rate = 160 mL/min.



Figure 11. (A) Dependence of the rate of C₄ product formation on the AcH partial pressure, measured at 573, 553, and 533 K with 2.73 kPa EtOH. (B) Effects of EtOH partial pressure on the rate of C₄ product formation, measured at 593, 573, and 563 K with 0.32 kPa AcH. The solid lines are fittings to eq 5. (C) Difference of the C₄ product formation rates between AcH aldol condensation and EtOH–AcH conversion with 2.73 kPa EtOH. (D) Comparison of the C₄ product formation rates from AcH aldol condensation and EtOH–AcH conversion at AcH partial pressures below 0.1 and 2.73 kPa EtOH. The solid lines in panels (A)–(D) are guides for eyes. Reaction conditions: 533–593 K, $m_{cat} = 10$ mg of 0.06La-DeAlBEA, and total flow rate = 80 mL/min.

similar carbon-based flow rate (0.087 mmol/ g_{cat} /min), indicating that the C–C bond formation process is the ratelimiting step for AcH–EtOH conversion to 1,3-BD over La-DeAlBEA.

As discussed before, both the MPV reaction and crotyl alcohol dehydration are facile over La-DeAlBEA, and C–C bond formation is the rate-limiting step. Therefore, the rate enhancement observed upon cofeeding EtOH and AcH suggests that EtOH reacts directly with AcH to form a C–C bond during 1,3-BD synthesis over La-DeAlBEA, as was

proposed for the occurrence of this reaction over isolated Y sites in Y-DeAlBEA.³

The experiments involving the conversion of reaction intermediates and switching of reactants suggest that the grafted (\equiv SiO)₂La-OH···HO-Si \equiv groups present in La-DeAlBEA are responsible for catalyzing AcH aldol condensation, the MPV reaction, and crotyl alcohol dehydration. Moreover, the silanol nests in DeAlBEA can also promote crotyl alcohol dehydration. When EtOH is cofed with AcH, C₄ product formation is enhanced by 4.8-fold, which is attributed



Scheme 2. Illustration of AcH and EtOH-AcH Mixture Conversion over Isolated La Sites Supported on DeAlBEA

to the opening up of a new C–C formation pathway involving EtOH and AcH. Comparing EtOH–AcH conversion over 0.06La-DeAlBEA and 0.85 wt %La-SiO₂, the new C–C bond formation route is found to be closely related to the H-bonding interaction between La–OH sites and silanol groups presented in DeAlBEA ((\equiv SiO)₂La–OH···HO–Si \equiv). Considering the description of the chemical structure and local environment of La sites over these two supports (DeAlBEA and SiO₂), a plausible explanation is that the Lewis acidic La center catalyzes C–C bond formation from AcH via aldol condensation, while the weak Brønsted acidity arising from the H-bonding La–OH and silanol groups (\equiv SiO)₂La–OH····HO–Si \equiv in La-DeAlBEA contributes to C–C bond formation between EtOH and AcH.

To further understand the two C-C formation processes, the kinetics of AcH aldol condensation and EtOH-AcH to 1,3-BD were investigated over La-DeAlBEA. The kinetics of AcH aldol condensation were explored by varying the AcH partial pressure and the reaction temperature while maintaining a constant total flow rate. In these experiments, crotonaldehyde was observed as the only product, and catalyst deactivation did not exceed 10% after testing under all reaction conditions. The conversion of AcH was kept below 10% at the lowest AcH partial pressure and the highest temperature to achieve close differential conditions. Under these conditions, the rate of crotonaldehyde formation is independent of the spacetime (Figure S11A). As shown in Figure 10A, the rate of crotonaldehyde formation is first-order in AcH partial pressure (<1.0 kPa) for all reaction conditions tested. A nearly firstorder dependence suggests that the adsorption of AcH over isolated La sites is weak and that enolization of AcH is most likely the rate-limiting step in aldol condensation, in agreement with previous studies over hydroxyapatite and ZrO₂/SiO₂.^{4,10} The rate expression for AcH aldol condensation without EtOH cofeeding presented as eq 3 below was derived with the following assumptions: the adsorption and desorption of AcH and crotonaldehyde are quasi-equilibrated; the concentration of intermediate species and AcH on the surface is negligible

and the formation of AcH enolate is rate-limiting. Equation 3 was fitted to the measured rate data shown in Figure 10A to obtain the apparent first-order rate coefficients $(k_1 * K_{AcH})$ for AcH aldol condensation. From an Arrhenius plot of the rate coefficient (Figure 10B), the experimentally measured apparent activation energy for AcH aldol condensation is estimated to be 26.8 kJ/mol.

The effects of the partial pressures of EtOH and AcH on the rates of C-C formation over isolated La sites on La-DeAlBEA were also explored, and the results are shown in Figure 11. For investigation of the effects of AcH partial pressure, EtOH and AcH were cofed with the EtOH partial pressure held constant at 2.73 kPa, while the partial pressure of AcH was varied from 0.055 to 0.505 kPa. The conversions of EtOH and AcH were kept below 8 and 25%, respectively, for all reaction conditions tested. Spacetime investigation of EtOH-AcH conversion (Figure S11B,C) indicates that the rate of C_4 product formation is independent of the space velocity. As shown in Figure 11A, the increase in AcH partial pressure leads to a rapid increase in the formation rate of all C₄ products including 1,3-BD and small amounts of butenes and crotyl alcohol (3%-15% of the total rate of C₄ product formation) for temperatures of 533, 553, and 573 K. Notably, the rate of C₄ product formation increases remarkably for AcH partial pressures <0.32 kPa and then increases further but at a lower rate for higher AcH partial pressures. At AcH partial pressures >0.40 kPa, the dependence on AcH partial pressure decreases to nearly zero order, as expected, because AcH eventually saturates the H-bonded $(\equiv SiO)_2La - OH - Si \equiv sites$.

As demonstrated above, EtOH is involved directly in C–C bond formation, and the rate of 1,3-BD formation via the reaction of EtOH and AcH is 4.8 times that observed in the absence of EtOH at 573 K with 0.42 kPa AcH. The dependence of the rates of C_4 product formation on EtOH partial pressure was then investigated for a constant AcH partial pressure of 0.32 kPa at 563, 573, and 593 K. Figure 11B shows that the rates of C_4 product formation increase almost linearly with increasing EtOH partial pressure up to about 1.3

kPa and then increase but at a lower rate for higher EtOH partial pressures. Generally, the rate of C–C bond formation increases with both EtOH and AcH partial pressures, consistent with the behavior found for Y-DeAlBEA.³ The rate of direct coupling between AcH and EtOH is expected to be zero to positive order in AcH and EtOH partial pressure, respectively, which also agrees with the experimental results shown in Figure 11A,B.

In summary, the overall rate of C-C bond formation is due to both AcH aldol condensation and direct EtOH-AcH coupling, the contribution of each process varying with the partial pressure of EtOH and AcH. The difference of C4 product formation rates between EtOH-AcH mixture conversion and pure AcH conversion as functions of AcH partial pressure and temperature is shown in Figure 11C. As the AcH partial pressure increases from 0.05 kPa to around 0.3 kPa, the fraction of C₄ products formed from EtOH-AcH conversion compared to AcH condensation without EtOH cofeeding increases monotonically and then reaches a plateau for higher AcH partial pressures. It is notable that the rate of C₄ product formation from EtOH–AcH conversion is slightly lower relative to the rate of AcH aldol condensation during pure AcH conversion for AcH partial pressures below 0.05 kPa (Figure 11C, D). This observation is attributed to the competitive adsorption of EtOH at remarkably lower AcH partial pressures, which inhibits both the rates of AcH aldol condensation and EtOH-AcH direct coupling. With further increase in the AcH partial pressure up to 0.5 kPa, both AcH aldol condensation and direct EtOH-AcH coupling contribute to the formation of C4 products. Figure 11C clearly shows that direct EtOH-AcH coupling is the main pathway for C-C bond formation at a constant EtOH partial pressure of 2.73 kPa and an AcH partial pressure of <0.5 kPa. Above an AcH partial pressure of 0.5 kPa, the difference in the rate of C₄ product formation between EtOH-AcH condensation and AcH aldol condensation reaches a plateau. It is hypothesized that at higher AcH concentrations, EtOH-AcH coupling may become inhibited due to the competitive adsorption of AcH.

Based on the reaction intermediates identified, the mechanism for the conversion of EtOH and AcH to 1,3-BD is envisioned to proceed, as illustrated in Scheme 2. The reaction process comprises two reaction cycles. In Cycle I, 1,3-BD is formed via aldol condensation of AcH over Lewis acid La sites, whereas in Cycle II, 1,3-BD proceeds via EtOH-AcH coupling over H-bonding $(\equiv SiO)_2La - OH - HO - Si \equiv$ sites. Sushkevich and Ivanova have reported that aldol condensation follows a stepwise pathway involving intermediate enol formation over Lewis acid Zr catalysts.⁴ Accordingly, Cycle I begins with AcH adsorption on the Lewis acid La sites and involves interaction of the nucleophilic oxygen of the carbonyl group with the electrophilic La, as depicted in Step I-1, Scheme 2.³⁴ Polarization of the carbonyl group in AcH is envisioned to enhance the acidity of the α -H (in the methyl group of adsorbed AcH) and therefore facilitates the α -H abstraction by the Lewis basic hydroxyl oxygen (La-OH) to form AcH enolate. Studies of butanal self-condensation over isolated Ti-OH species 68 and EtOH conversion to but adiene over Ag/ $\rm ZrO_2/SiO_2^{-4}$ have reported a kinetic H/D isotope effect for both reactions, suggesting that α -H abstraction is the ratelimiting step (Step I-3) for aldol condensation. Consistent with these findings, the kinetics of AcH aldol condensation are firstorder in AcH partial pressure, implying that enolate formation (rather than C-C coupling) is rate-limiting. Due to the

absence of strong basic sites, the enolate intermediate is likely stabilized via coordination to weak basic oxygen atoms associated with La, as suggested for Zr-SiO₂ and ZrBEA.^{4,7} Subsequently, adsorption of the second AcH molecule results in the formation of a penta-coordinated species. C-C coupling of the nucleophilic carbon of the enolate intermediate with the electrophilic carbonyl carbon of the secondary adsorbed AcH forms acetaldol (Step I-5), which dehydrates rapidly to produce crotonaldehyde (Step I-6), as evidenced by the absence of acetaldol during AcH conversion. In the presence of EtOH, crotonaldehyde is envisioned to undergo rapid hydrogenation to crotyl alcohol via MPV hydrogen transfer from EtOH over La sites (Step I-7). Subsequent dehydration of crotyl alcohol (Step I-8) forms 1,3-BD (Step I-9) and another molecule of AcH. The direct coupling of EtOH-AcH (Cycle II) is envisioned to start with the stepwise adsorption of AcH and EtOH over Lewis acid La sites via an acid-base interaction (Step II-2 and Step II-3), similar to that proposed for Y-DeAlBEA.³ After that, concerted H abstraction of adsorbed AcH by the basic oxygen atom in the La-OH group and protonation of the carbonyl oxygen of AcH by the hydrogen atom of the H-bonded La-OH group are thought to occur (Step II-3), resulting in the formation of AcH enolate species. The next step is the rate-limiting C-C bond formation via the reaction of α -C in EtOH with α -C in AcH (Step II-4). This step is proposed based on exploration of the positive effects of AcH and EtOH partial pressures on the rate of 1,3-BD formation. The following step involves cleavage of the α C-H group in EtOH and H transfer to the enolate intermediate, as well as dehydration to form crotyl alcohol (Step II-5). Finally, dehydration of crotyl alcohol over (\equiv $SiO)_2La-OH\cdots HO-Si \equiv$ site produces 1,3-BD, completing the reaction cycle (Step II-6).

The mechanism presented in Scheme 2 allows us to derive two rate expressions for the C_4 product formation (see SI for details). Equation 1 is derived for the case in which the C–C bond formation is realized via AcH aldol condensation taking the formation of enol of AcH as the rate-limiting step, and eq 2 is derived for the case in which the C–C bond is formed by direct coupling of EtOH and AcH.³ In both cases, the adsorption and desorption of reactants are assumed to be quasi-equilibrated, and the surface coverages of intermediates are taken to be insignificant under differential reaction conditions.

 $r_{\rm AcH-AcH}$

$$=\frac{k_1 K_{AcH} P_{AcH}}{1 + K_{EtOH} P_{EtOH} + K_{AcH} P_{AcH} + K_{AA} K_{AcH} [P_{AcH}]^2 + K_Y P_{EtOH} P_{AcH}}$$
(1)

r_{AcH-EtOH}

$$=\frac{k_{\rm Y}K_{\rm Y}P_{\rm EtOH}P_{\rm AcH}}{1+K_{\rm EtOH}P_{\rm EtOH}+K_{\rm AcH}P_{\rm AcH}+K_{\rm AA}K_{\rm AcH}[P_{\rm AcH}]^2+K_{\rm Y}P_{\rm EtOH}P_{\rm AcH}}$$
(2)

In eq 1, the parameter k_1 is the rate coefficient for the formation of AcH enolate; P_{AcH} and P_{EtOH} are the partial pressures of AcH and EtOH; K_{AcH} and K_{EtOH} are the equilibrium constants for AcH and EtOH adsorption onto H-bonded (\equiv SiO)₂La-OH···HO-Si \equiv sites; K_Y is the equilibrium constant for EtOH and AcH coadsorption; and K_{AA} is the equilibrium constant for coadsorption of two AcH molecules. The inhibition of adsorbed AcH and product crotonaldehyde molecules is expected to be insignificant due to

the low AcH partial pressure and differential reaction conditions. For the C–C bond formation between EtOH and AcH (eq 2), $k_{\rm Y}$ represents the rate coefficient for the direct C–C coupling of AcH and EtOH.

When pure AcH is fed, the rate of C–C coupling is the aldol condensation rate, and eq 1 simplifies to eq 3. In the case when EtOH and AcH are cofed, the rate of C–C coupling is the sum of the two reaction pathways, and the rate expression is given by eq 4.

$$r_{C-C \text{ coupling}}^{A-A} = k_{I}K_{AcH}P_{AcH}$$

$$= \frac{k_{I}K_{AcH}P_{AcH} + k_{Y}K_{Y}P_{EtOH}P_{AcH}}{k_{I}K_{AcH}P_{AcH} + k_{Y}K_{Y}P_{EtOH}P_{AcH}}$$
(3)

$$\overline{1 + K_{\text{EtOH}}P_{\text{EtOH}} + K_{\text{A}}P_{\text{AcH}} + K_{\text{AA}}K_{\text{AcH}}[P_{\text{AcH}}]^2 + K_{\text{Y}}P_{\text{EtOH}}P_{\text{AcH}}}}$$
(4)

$$r_{\rm C-C\ coupling}^{\rm A-E} = \frac{k_{\rm I}K_{\rm AcH}P_{\rm AcH} + k_{\rm Y}K_{\rm Y}P_{\rm EtOH}P_{\rm AcH}}{1 + K_{\rm EtOH}P_{\rm EtOH} + K_{\rm Y}P_{\rm EtOH}P_{\rm AcH}}$$
(5)

$$r_{\rm C-C\ coupling}^{\rm A-E} = k_{\rm I} K_{\rm AcH} P_{\rm AcH} + k_{\rm Y} K_{\rm Y} P_{\rm AcH} P_{\rm EtOH}$$
(6)

$$r_{C-C \text{ coupling}}^{A-E} = \frac{k_{I}K_{ACH}P_{ACH}}{(K_{EtOH} + K_{Y}P_{ACH})P_{EtOH}} + \frac{k_{Y}K_{Y}P_{AcH}}{K_{EtOH} + K_{Y}P_{AcH}}$$
(7)

Equation 3 was fitted to the measured rate data shown in Figure 10A to obtain the apparent first-order rate coefficients $(k_1^*K_{ACH})$ for AcH aldol condensation, and the fitted results are listed in Table 3. Figure 12A shows the parity plot and the

 Table 3. Rate Parameters for C4 Product Formation from

 AcH Conversion over La-DeAlBEA

entry	first-order coefficient, mol mol $La^{1-} s^{-1} kPa^{-1}$			apparent E _a , kJ/mol	
temperature, K	513	533	553	573	
$k_1 K_{AcH}$	0.0267	0.0331	0.0415	0.0515	
E_{a}					26.8

value of R^2 is 0.99, suggesting the accurate description of eq 3 to AcH aldol condensation rates obtained experimentally. From an Arrhenius plot of the rate coefficient (Figure 10B), the experimentally measured apparent activation energy for

Since the rate of AcH aldol condensation has a first-order dependence on the AcH partial pressure, the third term $(K_A P_{AcH})$ and the fourth term $(K_{AA} K_{AcH} [P_{AcH}]^2)$ in the denominator of eq 4 are taken to be insignificant and, hence, eq 4 can be simplified to eq 5. Moreover, at a constant AcH partial pressure, for low EtOH partial pressures, the second term $(K_{EtOH}P_{EtOH})$ and the third term $(K_YP_{EtOH}P_{AcH})$ in the denominator of eq 5 can also be assumed to be negligible, and eq 5 can be further simplified to eq 6, which suggests the rate of C-C coupling is first-order in EtOH partial pressure. As the EtOH partial pressure increases to much higher values, $K_{\rm EtOH}P_{\rm EtOH}$ and $K_{\rm Y}P_{\rm EtOH}P_{\rm AcH}$ are expected to be much larger than 1, and eq 5 can thus be simplified further to eq 7. At a constant low AcH partial pressure, the second term, $\frac{k_Y K_Y P_{AcH}}{K_{EIOH}+K_Y P_{AcH}}$, is constant, and the first term in eq 7 decreases gradually as the EtOH partial pressure increases, reaching a plateau at higher EtOH partial pressures. Overall, eq 5 agrees very well with the experimental results, increasing linearly at lower EtOH partial pressures and then gradually reaching a plateau at much higher EtOH partial pressures (see Figure 11B).

Equation 5 was fitted to the measured rate data in Figure 11B by nonlinear least-squares regression. The fitted rate parameters are given in Table 4. The quality of the fit is high,

 Table 4. Rate Parameters for C₄ Product Formation from

 AcH-EtOH Conversion over La-DeAlBEA

	rate parameter	$K_{\rm E}$	$K_{ m Y}$	$k_{ m Y}$
Т, К	563	0.37	0.35	0.31
	573	0.30	0.29	0.45
	593	0.22	0.17	0.80
enthalpy (kJ/mol)	EtOH adsorption $\Delta H_{ m ads}({ m EtOH})$	-47.5		
	AcH-EtOH coadsorption $\Delta H_{ads}(AcH-EtOH)$		-67.9	
	intrinsic <i>E</i> _a (kJ/mol)			86.9



Figure 12. Parity plots for (A) aldol condensation rate of AcH and (B) formation rate of C_4 products from AcH–EtOH conversion obtained experimentally and fitted from eqs 3 and 5.

as can be judged by the parity plot shown in Figure 12B (the value of R^2 is 0.98). The estimated enthalpy for adsorption of EtOH (ΔH_{ads}) is -47.5 kJ/mol, and the enthalpy for coadsorption of EtOH and AcH is -67.9 kJ/mol. The intrinsic activation energy for the concerted EtOH and AcH C-C coupling step is around 86.9 kJ/mol. The adsorption energy of AcH over the isolated $(\equiv SiO)_2$ -Y-OH site has been reported to be -102.3 kJ/mol and the activation barrier for aldol condensation to be 157.3 kJ/mol over these sites.⁶⁹ Over the isolated $(\equiv SiO)_2$ -La-OH site, the experimentally measured apparent activation energy for AcH aldol condensation is about 26.8 kJ/mol. Considering the slightly lower Lewis acidity of La sites compared to Y sites, the adsorption enthalpy for AcH on the Lewis acid La center should be lower (i.e., more positive, > -102.3 kJ/mol) than that for Y Lewis sites. On that basis, the intrinsic activation barrier for AcH aldol condensation over isolated $(\equiv Si - O - La)_2 - OH$ sites is estimated to be around <129.1 kJ/mol. The intrinsic activation energy for EtOH and AcH C-C coupling, 86.9 kJ/mol, is most likely lower than that for AcH adol condensation.

CONCLUSIONS

An investigation was conducted of the reaction mechanism and kinetics of EtOH and AcH conversion to 1,3-BD over isolated Lewis acid La sites grafted into the silanol nests of dealuminated Beta zeolite. La-DeAlBEA prepared with La/Al < 0.24 characterized by IR spectroscopy of adsorbed pyridine, deuterated acetonitrile, and DTBPy and XAS reveals that La is present as isolated sites with a structure of $(\equiv SiO)_2La-OH\cdots$ HO-Si≡, a structure containing both Lewis acidic La sites and weak Brønsted acidic sites. On the other hand, isolated La sites grafted onto the isolated silanol groups over SiO₂ are present only in the form of $(\equiv SiO)_2La-OH$, with no evidence that La-OH groups are H-bonded with adjacent Si-OH groups. Investigation of the mechanism and kinetics of AcH coupling over isolated La-DeAlBEA shows that Lewis acid La sites catalyze C-C coupling and MPV hydrogen transfer, whereas weakly Brønsted acid sites associated with ≡SiOH groups interacting with Lewis acid La sites and unconsumed silanol nests contribute to the dehydration of crotyl alcohol. It is notable that isolated La sites on both La-DeAlBEA and La-SiO₂ exhibit similar AcH aldol condensation rates, supporting the conclusion that Lewis acid La sites catalyze C-C coupling. An increase in the rate of 1,3-BD formation by a factor of 4.8 was observed upon addition of EtOH to AcH fed over La-DeAlBEA, whereas the rate of C₄ product formation over La-SiO₂ was not affected by the addition of EtOH. Combined with the similar chemical structure of La sites for both La-DeAlBEA and La-SiO₂, this difference in catalytic behavior is ascribed to the presence of H-bonding interaction between La-OH groups and proximal silanol groups in La-DeAlBEA. The rate of crotonaldehyde formation via AcH aldol condensation over La-DeAlBEA exhibits close to first-order dependence on AcH partial pressure, suggesting that the enolization of AcH is the most likely rate-limiting step in aldol condensation. In the case of EtOH-AcH conversion to 1,3-BD, both EtOH and AcH exhibit a positive order dependence, implying that both EtOH and AcH are involved in the new C-C bond formation pathway. The results of this work provide critical insight into the development of active catalysts for the conversion of EtOH to 1.3-BD.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.4c03935.

Experimental methods; IR result of dealumination of H-BEA; ICP and XRD results of La-DeAlBEA; plots of integrated peak area for pyridine adsorption bands versus La/Al ratio for La-DeAlBEA; changes of IR spectra for CD₃CN and pyridine adsorption with purging time; ¹H NMR spectra and spectral deconvolution; changes of k-space and R-space data before and after MEE removal treatment of 0.06La-DeAlBEA and 0.85 wt %La-SiO₂; formation rates of C₄ products with TOS over La-SiO₂; spacetime investigation of AcH aldol condensation and EtOH–AcH conversion; and derivation of the expressions of the rates of C₄ product formation from AcH aldol condensation (PDF)

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Notes

The authors declare no competing financial interest.

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