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# Mechanism and Kinetics of Propane Dehydrogenation and Cracking over Ga/H-MFI Prepared via Vapor-Phase Exchange of H-MFI with GaCl<sub>3</sub>

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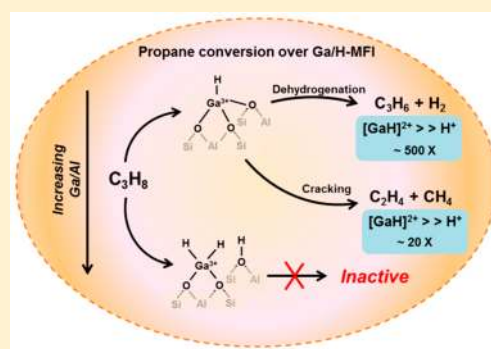
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## Supporting Information

**ABSTRACT:** In this study, the mechanism and kinetics of C<sub>3</sub>H<sub>8</sub> dehydrogenation and cracking are examined over Ga/H-MFI catalysts prepared via vapor-phase exchange of H-MFI with GaCl<sub>3</sub>. The present study demonstrates that [GaH]<sup>2+</sup> cations are the active centers for C<sub>3</sub>H<sub>8</sub> dehydrogenation and cracking, independent of the Ga/Al ratio. For identical reaction conditions, [GaH]<sup>2+</sup> cations in Ga/H-MFI exhibit a turnover frequency for C<sub>3</sub>H<sub>8</sub> dehydrogenation that is 2 orders of magnitude higher and for C<sub>3</sub>H<sub>8</sub> cracking, that is 1 order of magnitude higher than the corresponding turnover frequencies over H-MFI. C<sub>3</sub>H<sub>8</sub> dehydrogenation and cracking exhibit first-order kinetics with respect to C<sub>3</sub>H<sub>8</sub> over H-MFI, but both reactions exhibit first-order kinetics over Ga/H-MFI only at very low C<sub>3</sub>H<sub>8</sub> partial pressures and zero-order kinetics at higher C<sub>3</sub>H<sub>8</sub> partial pressures. H<sub>2</sub> inhibits both reactions over Ga/H-MFI. It is also found that the ratio of the rate of dehydrogenation to the rate of cracking over Ga/H-MFI is independent of C<sub>3</sub>H<sub>8</sub> and H<sub>2</sub> partial pressures but weakly dependent on temperature. Measured activation enthalpies together with theoretical analysis are consistent with a mechanism in which both the dehydrogenation and cracking of C<sub>3</sub>H<sub>8</sub> proceed over Ga/H-MFI via reversible, heterolytic dissociation of C<sub>3</sub>H<sub>8</sub> at [GaH]<sup>2+</sup> sites to form [C<sub>3</sub>H<sub>7</sub>-GaH]<sup>+</sup>-H<sup>+</sup> cation pairs. The rate-determining step for dehydrogenation is the β-hydride elimination of C<sub>3</sub>H<sub>6</sub> and H<sub>2</sub> from the C<sub>3</sub>H<sub>7</sub> fragment. The rate-determining step for cracking is C–C bond attack of the same propyl fragment by the proximal Brønsted acid O–H group. H<sub>2</sub> inhibits both dehydrogenation and cracking over Ga/H-MFI via reaction with [GaH]<sup>2+</sup> cations to form [GaH<sub>2</sub>]<sup>+</sup>-H<sup>+</sup> cation pairs.



## 1. INTRODUCTION

The increasing availability of large shale gas reserves in the U.S. and across the world has stimulated interest in finding routes for the catalytic conversion of the condensable components of shale gas, principally ethane and propane, to alkenes and aromatics via dehydrogenation and dehydrocyclization, respectively.<sup>1–5</sup> Commercially implemented processes<sup>6</sup> include the Oleflex and Catofin processes for dehydrogenation, which utilize alumina-supported catalysts and also the Cyclar and Aroforming processes, which use metal-modified zeolite catalysts for dehydroaromatization. Gallium-exchanged H-MFI zeolite (Ga/H-MFI) has been shown to be particularly effective for catalyzing alkane dehydroaromatization.<sup>5,7–11</sup> For example, reactions of C<sub>3</sub>H<sub>8</sub> over Ga/H-MFI result in higher selectivities to alkenes and aromatics than those observed over unmodified H-MFI.<sup>10,12</sup> This has led to a renewed interest in studying the structure and catalytic role of Ga species in Ga/H-MFI, as active sites for light alkane conversion.<sup>13–22</sup>

The chemical structure and catalytic function of Ga cations in Ga/H-MFI have been examined both experimentally and

theoretically.<sup>23</sup> These studies suggest that in the oxidized or reduced state, the following types of species may exist in Ga/H-MFI: [GaO]<sup>+</sup>, [Ga<sub>2</sub>O<sub>2</sub>]<sup>+</sup>, [Ga(OH)]<sup>2+</sup>, [Ga(OH)<sub>2</sub>]<sup>+</sup>, [GaH<sub>2</sub>]<sup>+</sup>, [GaH]<sup>2+</sup>, Ga<sup>+</sup>, and GaO<sub>x</sub> clusters.<sup>9,24–32</sup> It should be noted that with the exception of Ga<sup>+</sup>, the oxidation state of Ga in all of the other proposed structures is +3. Earlier studies of light alkane dehydrogenation over Ga/H-MFI have reported that oxygen-ligated species, such as monomeric [GaO]<sup>+</sup> or dimeric [Ga<sub>2</sub>O<sub>2</sub>]<sup>2+</sup> cations, are more active than reduced Ga<sup>+</sup> cations.<sup>26,29–31</sup> However, contemporaneous studies as well as more recent ones have suggested that Ga<sup>+</sup> cations are the active centers for alkane dehydrogenation.<sup>9,10,15,28,29,33,34</sup> A variant of this idea has also been recently proposed, namely, that Ga<sup>+</sup> cations in proximity to Brønsted acid O–H groups catalyze C<sub>3</sub>H<sub>8</sub> dehydrogenation via oxidative addition of H<sup>+</sup> to Ga<sup>+</sup> to form a highly Lewis acidic [GaH]<sup>2+</sup> species in which the Ga<sup>3+</sup> center has an oxidation state of +3.<sup>22</sup> The role of [GaH]<sup>2+</sup>

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cations as the active center for alkane dehydrogenation has also been supported by theoretical studies. These studies show that divalent  $[\text{GaH}]^{2+}$  cations, located at proximate cation-exchange sites in Ga/H-MFI, are more active for light alkane dehydrogenation than monovalent  $[\text{GaH}_2]^+$  cations or  $\text{Ga}^+$  cations.<sup>22,32,35,36</sup>

While a number of authors have proposed that  $\text{Ga}^+$  cations are active for the dehydrogenation of light alkanes,<sup>9,10,15,28,29,33,34,37</sup> the presence of  $\text{Ga}^+$  cations in  $\text{H}_2$ -reduced Ga/H-MFI has been disputed. Recent work by Getsoian et al. has called into question the interpretation of XANES evidence for  $\text{Ga}^+$  cations.<sup>18</sup> These authors note that the decreases in the Ga K-edge XANES edge energy of Ga/H-MFI upon reduction, previously ascribed to formation of  $\text{Ga}^+$ ,<sup>9,10</sup> can be ascribed, instead, to the formation of Ga-alkyl or  $\text{GaH}_x$  species, in which Ga has a formal oxidation state of +3.<sup>18</sup> Theoretical studies have also shown that the activation barrier for the formation of  $\text{Ga}^+$  species in Ga/H-MFI is considerably higher than that for the formation of  $\text{GaH}_x$  species in which the Ga center has a formal oxidation state of +3.<sup>36,38</sup>

A further issue complicating the identification of the catalytically active species in Ga/H-MFI is the synthetic protocol typically employed for the preparation of Ga/H-MFI: incipient wetness impregnation of H-MFI with an aqueous solution of a Ga salt, most notably  $\text{Ga}(\text{NO}_3)_3$ .<sup>39</sup> Steric and electronic constraints associated with large aqueous  $\text{Ga}^{3+}$  complexes result in a slow diffusion of Ga into the MFI micropores, leading to low levels of ion exchange and the deposition of  $\text{GaO}_x$  agglomerates at the external surfaces of the zeolite crystal.<sup>23,40</sup> Upon contact with  $\text{H}_2$  or alkane reactants at reaction temperatures ( $>700$  K), ion exchange has been reported to occur via conversion of  $\text{GaO}_x$  into volatile  $\text{Ga}_2\text{O}$  monomers.<sup>9</sup> However, the resulting materials have been reported to still contain detectable concentrations of  $\text{GaO}_x$ .<sup>40</sup> The presence of neutral  $\text{GaO}_x$  together with ion-exchanged  $\text{Ga}^{3+}$  cations in Ga/H-MFI prepared via the conventional protocol has precluded accurate determination of the active Ga structures and their catalytic role in light alkane dehydrogenation and dehydroaromatization.

We report here a detailed study of the mechanism and kinetics of  $\text{C}_3\text{H}_8$  dehydrogenation and cracking over Ga/H-MFI with Ga/Al ratios ranging from 0.05 to 0.5. These catalysts were prepared by reaction of the Brønsted acid O–H groups in H-MFI with  $\text{GaCl}_3$  vapor under anhydrous conditions at elevated temperature, followed by stoichiometric removal of Ga-bound Cl by  $\text{H}_2$  reduction, resulting in the formation of  $\text{GaH}_x$  ( $x = 1, 2$ ) structures. Detailed characterization of these samples shows that for Ga/Al ratios below 0.3, and upon reduction under anhydrous conditions, all of the Ga is present as isolated  $[\text{GaH}]^{2+}$  cations or as  $[\text{GaH}_2]^+\text{-H}^+$  cation pairs; neutral  $\text{GaO}_x$  agglomerates are undetectable in these samples.<sup>41</sup> Both types of cationic species are associated with proximate cation-exchange sites associated with NNN (next nearest neighboring, i.e., separated by a –O–Si–O linkage) or NNNN (next, next nearest neighboring, i.e., separated by a –O–Si–O–Si–O linkage) pairs of framework Al atoms. Our investigations show that  $\text{C}_3\text{H}_8$  dehydrogenation over these samples of Ga/H-MFI occurs primarily over  $[\text{GaH}]^{2+}$  cations, independent of the Ga/Al ratio, at a rate (per  $\text{Al}_{\text{tot}}$  atom) that is 2 orders of magnitude higher than that occurring over isolated Brønsted acid O–H groups located in H-MFI, under identical reaction conditions. The rate of  $\text{C}_3\text{H}_8$  cracking to

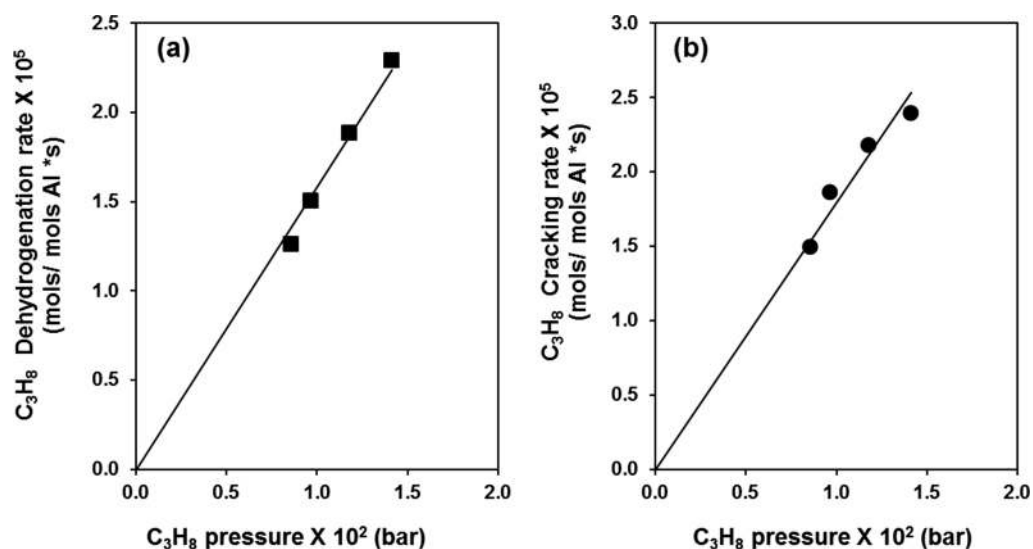
$\text{CH}_4$  and  $\text{C}_2\text{H}_4$  over Ga/H-MFI is an order of magnitude higher than that over H-MFI and also occurs over  $[\text{GaH}]^{2+}$  sites. While both cracking and dehydrogenation rates exhibit first-order dependences on  $\text{C}_3\text{H}_8$  partial pressure over H-MFI, the rates of both reactions exhibit a Langmuir–Hinshelwood dependence on  $\text{C}_3\text{H}_8$  partial pressure over Ga/H-MFI and are inhibited by  $\text{H}_2$ . Over H-MFI, both the dehydrogenation and cracking of  $\text{C}_3\text{H}_8$  occur over Brønsted acid O–H groups. In the case of Ga/H-MFI, examination of alternative reaction pathways via experiment and theory suggests that both reactions occur preferentially on  $[\text{GaH}]^{2+}$  sites via mechanisms involving  $\text{C}_3\text{H}_8$ -derived  $[\text{C}_3\text{H}_7\text{-GaH}]^+$  intermediates. Inhibition of both reactions by  $\text{H}_2$  is proposed to occur via the formation of  $[\text{GaH}_2]^+\text{-H}^+$  cation pairs.

## 2. EXPERIMENTAL AND THEORETICAL METHODS

**2.1. Preparation of H-MFI and Ga/H-MFI.**  $\text{NH}_4\text{-MFI}$  (Zeolyst, CBV 3024E) was converted to the H-form by heating it at  $2\text{ K min}^{-1}$  to 773 K in dry synthetic air (Praxair, ultrazero,  $100\text{ cm}^3\text{ min}^{-1}$ ) and then holding it at this temperature for 4 h. The  $\text{Si}/\text{Al}_{\text{tot}}$  ratio of this sample is  $16.5 \pm 1.0$ , as determined by ICP-OES (Galbraith Laboratories, Knoxville, TN, USA). Ga/H-MFI samples with varying Ga/Al ratios (0.05–0.5) were prepared via anhydrous exchange of dehydrated H-MFI with  $\text{GaCl}_3$  vapor, using a protocol developed by our group. A detailed discussion of the preparation and characterization of these samples is given in ref 41.

**2.2. Reaction Rate Measurements.** Reaction rates for  $\text{C}_3\text{H}_8$  conversion over H-MFI and Ga/H-MFI were measured using a tubular quartz plug flow reactor. Catalyst samples ( $\sim 5\text{--}12$  mg) were placed over a quartz wool plug, fitted inside the reactor (30.5 cm in length and 0.64 cm in outer diameter). Catalyst charges less than 8 mg were diluted with  $\text{SiO}_2$  (Silia Flash 150A). The reactor was heated by means of a ceramic cylindrical furnace. The temperature of the catalyst bed was measured by a K-type thermocouple (Omega) connected to a temperature controller (Omega), to maintain the catalyst temperature. Gases were metered into the reactor by means of mass flow controllers (MFCs) (Porter), which were calibrated using a bubble flow meter. Prior to making rate measurements, samples were heated at  $2\text{ K min}^{-1}$  from ambient temperatures to 773 K under flowing dry synthetic air (Praxair, ultrazero,  $100\text{ cm}^3\text{ min}^{-1}$ ) and held at this temperature for 1 h. This oxidative pretreatment was used for H-MFI and Ga/H-MFI. Reductive pretreatment of Ga/H-MFI was carried out by purging the system with He following the oxidative treatment at 773 K and then switching the reactor feed to a gas mixture of 2.5%  $\text{H}_2$  diluted in He (Praxair, CSG,  $100\text{ cm}^3\text{ min}^{-1}$ ). Samples were held at this temperature under  $\text{H}_2$  for 1 h.

Following either oxidative or reductive pretreatments, samples were exposed to flowing mixtures of  $\text{C}_3\text{H}_8/\text{He}$  prepared by diluting a 20%  $\text{C}_3\text{H}_8/\text{He}$  stream (Praxair, CSG) with He (Praxair, UHP) in order to generate  $\text{C}_3\text{H}_8$  partial pressures ranging from 0.25 to 11 kPa. Experiments involving co-fed  $\text{H}_2$  were conducted by adding  $\text{H}_2$  to the feed flow. For this purpose, a 2.5%  $\text{H}_2/\text{He}$  stream (Praxair, CSG) was mixed with the  $\text{C}_3\text{H}_8/\text{He}$  stream in order to obtain  $\text{H}_2$  partial pressures ranging from 0.25 to 1.5 kPa. The total pressure of the system was maintained at 101.32 kPa. He,  $\text{H}_2$ , and dry synthetic air were further purified by passing these gases through purifiers (VICI) in order to remove trace amounts of  $\text{H}_2\text{O}$  or hydrocarbons. Gas flow rates were varied ( $100\text{--}350\text{ cm}^3\text{ min}^{-1}$ ) in order to measure catalyst activity at different space times (defined as  $\text{mol Al}_{\text{tot}}\text{-s/mol C}_3\text{H}_8$ ) for a given  $\text{C}_3\text{H}_8/\text{H}_2/\text{He}$  feed composition. A heated line connected to the outlet of the reactor was used to transfer reactants and reaction products to a gas chromatograph (GC) (Agilent 7890A). The reactor effluent present in a sample loop was injected periodically into the GC. Reactants and products were separated by a capillary column (Agilent 1909IP-Q02,  $25\text{ m} \times 350\text{ }\mu\text{m} \times 10\text{ }\mu\text{m}$ ) and were detected by means of a flame ionization detector (FID). FID response factors for hydrocarbons species were obtained by diluting a precalibrated gas mixture containing  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_3\text{H}_6$ ,  $\text{C}_4\text{H}_{10}$ , and  $\text{C}_4\text{H}_8$



**Figure 1.** (a) Dependence of  $C_3H_8$  dehydrogenation rates (per  $Al_{tot}$  atom) on  $C_3H_8$  partial pressure measured over H-MFI at 733 K. (b) Dependence of  $C_3H_8$  cracking rates (per  $Al_{tot}$  atom) on  $C_3H_8$  partial pressure measured over H-MFI at 733 K. Solid lines indicate regressed first-order slopes.

with He to attain different concentrations of the component hydrocarbons. The response factors for  $C_6H_6$  and  $C_7H_8$  were determined by directly injecting known amounts of liquid  $C_6H_6$  and  $C_7H_8$  into the GC injector.

The conversion of  $C_3H_8$  over H-MFI and Ga/H-MFI was measured at differential conversions (<9%  $C_3H_8$  conversion) at temperatures between 718 and 753 K. Plots of conversion vs space time were linear for each feed composition combination and extrapolated to zero conversion at zero space time, consistent with reactor operation under a differential conversion regime. Selectivities were defined on both a C basis and  $C_3H_8$  basis.  $C_3H_8$  dehydrogenation rates were determined from  $C_3H_6$  concentrations, while  $C_3H_8$  cracking rates were determined from the concentrations of either  $CH_4$  or  $C_2H_4$  cracking products. When product selectivities were extrapolated to zero space time, cracking rates derived from  $CH_4$  concentrations were similar to those determined from  $C_2H_4$  concentrations. The  $C_3H_8$  partial pressures (0.25–11 kPa) and  $H_2$  partial pressures (0.25–1.5 kPa) were varied in a nonsystematic fashion in order to examine the effects of reactant and product pressures on measured rates. For each combination of  $C_3H_8/H_2$  partial pressures, rates were measured at four different space times. By this means, rates could be extrapolated linearly to 0 space time. Moreover, after measurements had been made at each  $C_3H_8/H_2$  pressure combination, rates were measured at 0.9 kPa  $C_3H_8/He$  at a space time of 9 mol Al-s/mol  $C_3H_8$  in order to assess and correct for catalyst deactivation. Catalyst deactivation did not exceed 5% in typical experiments. Activation enthalpies and entropies were extracted by relations (eqs S24–S26) derived from transition state theory.<sup>42</sup> For the application of these equations, rate coefficients (per  $Al_{tot}$  atom) were normalized by the fraction of  $[GaH]^{2+}$  cations per  $Al_{tot}$  atom determined via  $NH_3$ -TPD measurements (details described in the SI).<sup>41</sup>

**2.3. Theoretical Methods.** The hybrid quantum mechanics/molecular mechanics (QM/MM)<sup>43,44</sup> approach used in this work takes into account the impact of long-range dispersive interactions and the polarization of the active site by the electrostatic field associated with the zeolite lattice, both of which are critical to capturing reaction energetics accurately.<sup>45</sup> A T437 atom cluster was used to represent the zeolite framework surrounding the active site. The QM region consists of either a T5 or a T9 cluster representing the part of the zeolite associated with the extra-framework cation ( $H^+$  or  $[Ga(H)_n]^{(3-n)+}$ ) and any adsorbed species. The MM region was modeled with an improved parametrization;<sup>46</sup> framework Si and O atoms were fixed at their crystallographic positions. The framework Al

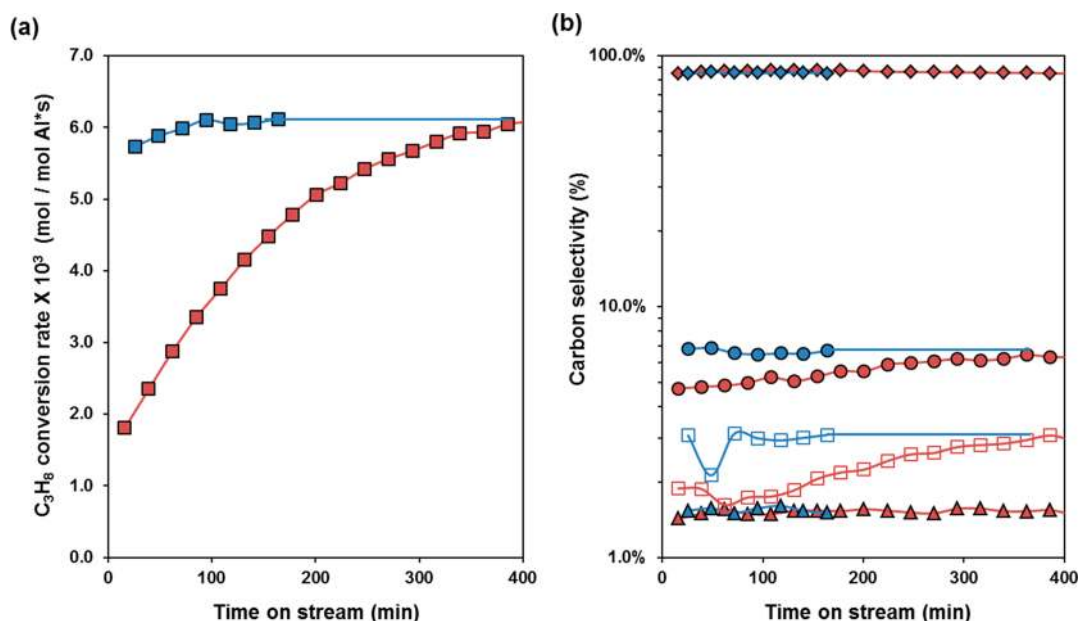
atom associated with extra-framework Ga cationic species was taken to be at the T12 site. This T site is located in the channel intersections of MFI.<sup>47</sup> The activities of both Brønsted acid O–H groups and Lewis acidic  $[GaH]^{2+}$  cations were investigated. As shown previously, only a small difference (2.6 kcal/mol) was found in the calculated barriers for  $C_2H_4$  methylation over H-MFI calculated for both T5 and T20 clusters,<sup>48</sup> which suggests that our QM/MM approach is not influenced significantly by the size of the QM region used. An illustration of the model used for the  $[GaH]^{2+}$  cation in this study is shown in Figure S.5 and is discussed in more detail in earlier work.<sup>36</sup>

Stationary and saddle point searches were conducted at the  $\omega B97X-D/6-31G^{**}$  level of theory using the default optimization procedure available in QChem.<sup>49</sup> The reported activation energies were computed using the  $\omega B97X-D$  functional<sup>50</sup> with the triple- $\zeta$ , split-valence Pople basis set, with diffuse and polarization functions 6-311++G(3df,3pd). While recent developments in density functional theory (DFT) have led to functionals with statistically improved accuracy<sup>51,52</sup> relative to  $\omega B97X-D$ , we note that the QM/MM parameters were developed specifically for that functional. Enthalpy and entropy calculations were performed using the quasi rigid rotor harmonic oscillator (RRHO) approximation. We have used this approach successfully in previous studies to obtain activation enthalpies and entropies for n- $C_4H_{10}$  reactions in H-MFI, yielding good agreement with experimental results.<sup>53</sup> For each mechanism examined, we determined the value of  $\Delta G^\ddagger$  from the respective free energy surface using the energetic span model proposed by Kozuch and Shaik.<sup>54–57</sup>

### 3. RESULTS AND DISCUSSION

**3.1.  $C_3H_8$  Conversion over H-MFI via Monomolecular Dehydrogenation and Cracking.** For times-on-stream < 100 min, the rate of  $C_3H_8$  dehydrogenation over H-MFI decreased monotonically, before approaching a steady state (see Figure S.1). However, the rate of  $C_3H_8$  cracking did not change appreciably with time-on-stream. These trends are similar to those reported for n- $C_4H_{10}$  dehydrogenation and cracking over H-MFI.<sup>58</sup> The authors of that study proposed that the high initial rate of n- $C_4H_{10}$  dehydrogenation is attributable to Lewis acidic, extra-framework Al (EFAl) sites that deactivate during the first 100 min of reaction. All steady-state rates were therefore measured over H-MFI, after the deactivation period (~100 min).





**Figure 2.** (a) C<sub>3</sub>H<sub>8</sub> consumption rates (per Al<sub>tot</sub> atom) and (b) percent carbon selectivities for Ga/H-MFI (Ga/Al = 0.2) measured at 733 K with 0.9 kPa C<sub>3</sub>H<sub>8</sub>/He and  $\tau = 9$  (mol Al·s/mol C<sub>3</sub>H<sub>8</sub>) space time. Blue data points indicate Ga/H-MFI pretreated in 2.5% H<sub>2</sub>/He at 773 K for 1 h prior to reaction, while red data points indicate Ga/H-MFI pretreated in synthetic dry air at 773 K for 1 h prior to reaction. In Figure 2b, diamonds indicate C<sub>3</sub>H<sub>6</sub>, circles indicate C<sub>2</sub>H<sub>4</sub>, open squares indicate aromatics, and triangles indicate CH<sub>4</sub> selectivities.

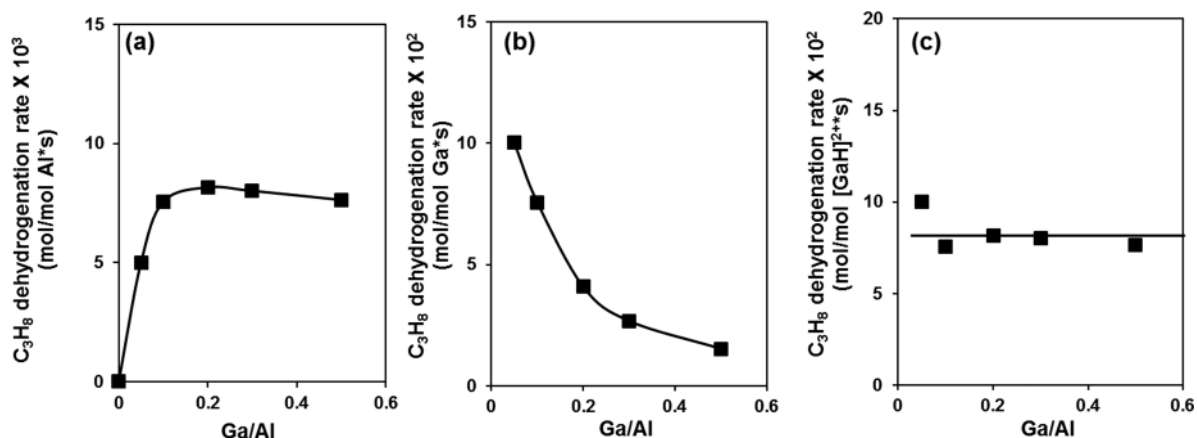
The steady-state product molar ratios of H<sub>2</sub>/C<sub>3</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub>/CH<sub>4</sub> during C<sub>3</sub>H<sub>8</sub> conversion over H-MFI were close to unity, consistent with previous studies of C<sub>3</sub>H<sub>8</sub> dehydrogenation and cracking over H-MFI.<sup>58–60</sup> As seen in Figure 1a and b, the rates of both dehydrogenation and cracking are first-order in C<sub>3</sub>H<sub>8</sub> partial pressure, also in agreement with previous reports for monomolecular dehydrogenation and cracking catalyzed by Brønsted acid O–H groups at low alkane partial pressures.<sup>61,62</sup>

Apparent first-order rate coefficients were measured at different temperatures (see Figure S.2.), and these data were used to determine apparent activation enthalpies ( $\Delta H_{app}$ ) for C<sub>3</sub>H<sub>8</sub> dehydrogenation and cracking. The experimentally measured apparent activation enthalpies for C<sub>3</sub>H<sub>8</sub> dehydrogenation and cracking were found to be  $40.6 \pm 2.9$  and  $34.6 \pm 3.8$  kcal/mol, respectively (reported uncertainties reflect 95% confidence intervals). Both estimates are consistent with previous reported estimates of activation energies for C<sub>3</sub>H<sub>8</sub> monomolecular dehydrogenation (22.7–47.8 kcal/mol) and monomolecular cracking (35.1–37.7 kcal/mol) over H-MFI.<sup>59,60,63,64</sup> We also obtained theoretical estimates of apparent activation enthalpies for these reactions occurring over isolated Brønsted acid O–H groups in H-MFI via QM/MM calculations. Apparent activation enthalpies estimated in this manner are 47.5 kcal/mol for methyl C–H activated C<sub>3</sub>H<sub>8</sub> dehydrogenation, 35.3 kcal/mol for methylene C–H activated C<sub>3</sub>H<sub>8</sub> dehydrogenation, and 33.3 kcal/mol for C<sub>3</sub>H<sub>8</sub> cracking. The activation enthalpy for methylene-C<sub>3</sub>H<sub>8</sub> dehydrogenation is expected to be significantly lower than that for methyl C<sub>3</sub>H<sub>8</sub>-dehydrogenation, due to the higher stability of the secondary carbenium ion formed in the late dehydrogenation transition state of the former pathway relative to the primary carbenium formed in the late dehydrogenation transition state of the latter pathway. Consistent with this interpretation, our experimental measurements are in good agreement with theoretical predictions for methylene dehydrogenation and cracking.

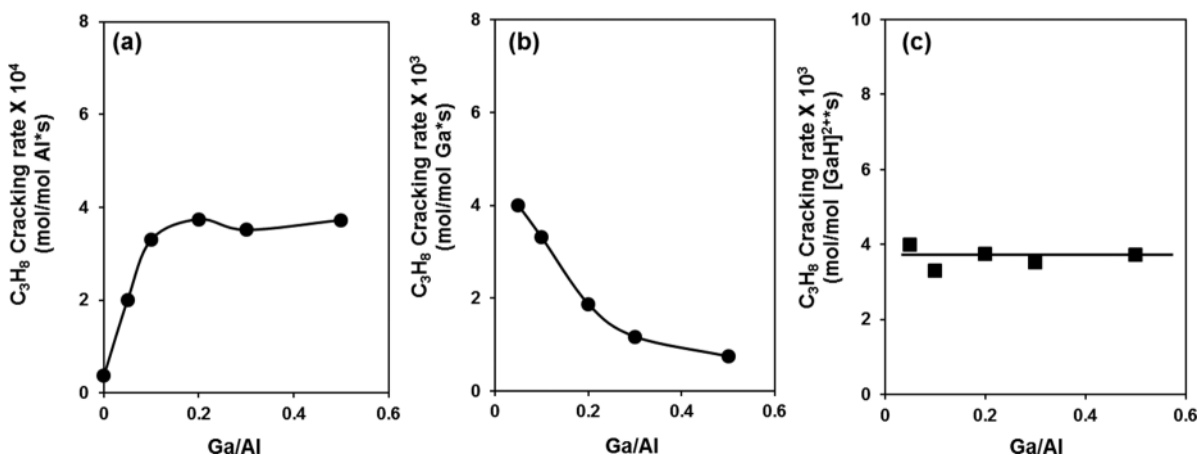
The transition state structures and free energy surfaces for these mechanisms are presented in Figures S.13 and S.14 of the SI.

**3.2. C<sub>3</sub>H<sub>8</sub> Conversion over Oxidized and H<sub>2</sub>-Reduced Ga/H-MFI.** Figure 2a shows the rates of C<sub>3</sub>H<sub>8</sub> consumption at 733 K over Ga/H-MFI (Ga/Al = 0.2) under differential reaction conditions (C<sub>3</sub>H<sub>8</sub> conversion <9%). Following oxidative pretreatment of Ga/H-MFI (at 773 K in flowing dry air for 1 h), the rate of C<sub>3</sub>H<sub>8</sub> consumption increases monotonically with time-on-stream for ~300 min before approaching a steady state (red curve, Figure 2a). This slow induction period suggests that Ga species undergo structural transformation before reaching their steady-state structure. Also shown in Figure 2a is the rate of C<sub>3</sub>H<sub>8</sub> consumption as a function of time-on-stream for Ga/H-MFI (Ga/Al = 0.2) reduced in 2.5% H<sub>2</sub>/He for 1 h at 773 K prior to measurements of the reaction rate (blue curve, Figure 2a). In this case, no induction period is observed and the steady-state rate of C<sub>3</sub>H<sub>8</sub> consumption is nearly identical to that measured over the oxidized sample.

Product selectivities (expressed as the fraction of converted carbon in each product) are shown as a function of time-on-stream in Figure 2b, for oxidized and H<sub>2</sub>-reduced Ga/H-MFI. Throughout the duration of the experiment, the dominant product is C<sub>3</sub>H<sub>6</sub>, produced via C<sub>3</sub>H<sub>8</sub> dehydrogenation. The selectivity to C<sub>3</sub>H<sub>6</sub> does not change with time-on-stream or catalyst pretreatment. The same is true for the selectivity to CH<sub>4</sub>. For the oxidized sample, the selectivities to C<sub>2</sub>H<sub>4</sub> and aromatics increase slightly as a function of time-on-stream, but approach the same values as that observed for the reduced sample. While C<sub>2</sub>H<sub>4</sub> is formed as a primary product via cracking of C<sub>3</sub>H<sub>8</sub>, space time studies (see Section S.3) indicate that C<sub>2</sub>H<sub>4</sub> is also produced via secondary pathways at higher conversions. These experiments also show that aromatics are produced exclusively via secondary pathways, which become increasingly prevalent at higher conversion. Therefore, the



**Figure 3.** C<sub>3</sub>H<sub>8</sub> dehydrogenation rates, measured at 0.9 kPa C<sub>3</sub>H<sub>8</sub>/He and 733 K as a function of Ga/Al ratio, with rates over Ga/H-MFI extrapolated to zero space time. (a) Rates normalized per Al<sub>tot</sub> atom. (b) Rates normalized per Ga atom. (c) Rates normalized per [GaH]<sup>2+</sup> estimated via NH<sub>3</sub>-TPD.<sup>41</sup> Solid lines are guides for the eye.



**Figure 4.** C<sub>3</sub>H<sub>8</sub> cracking rates over H-MFI and Ga/H-MFI, measured at 0.9 kPa C<sub>3</sub>H<sub>8</sub>/He and 733 K. Rates over Ga/H-MFI were extrapolated to zero space time. (a) Rates normalized per Al<sub>tot</sub> atom. (b) Rates normalized per Ga atom. (c) Rates normalized per [GaH]<sup>2+</sup> estimated via NH<sub>3</sub>-TPD measurements. Dotted lines are guides for the eye.

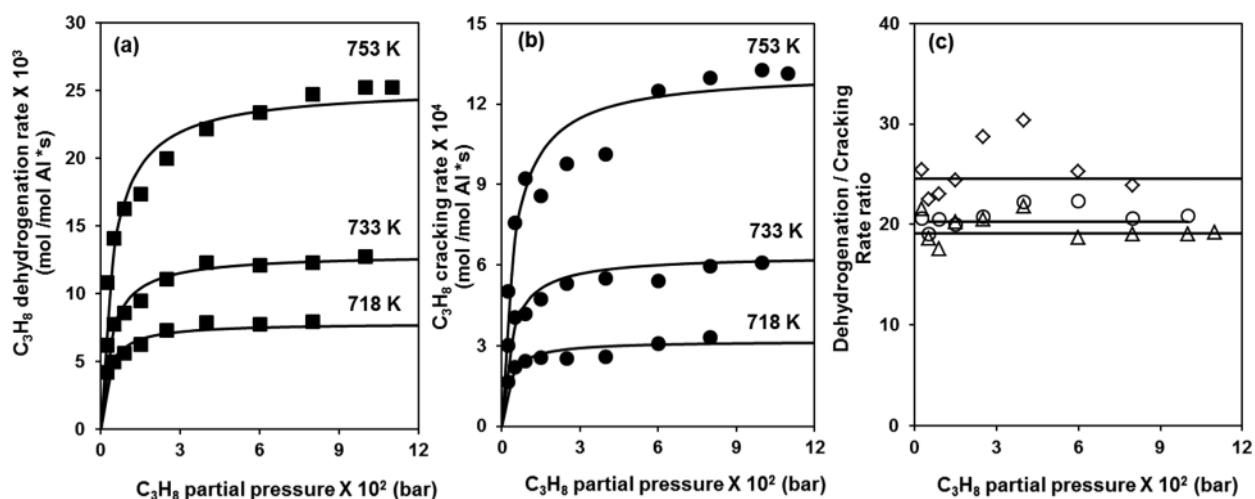
concentrations of both C<sub>2</sub>H<sub>4</sub> and aromatics are expected to increase as the rate of C<sub>3</sub>H<sub>8</sub> consumption over oxidized Ga/H-MFI increases with time-on-stream. Thus, the product selectivity trends seen in Figure 2b suggest that similar active sites catalyze C<sub>3</sub>H<sub>8</sub> dehydrogenation and cracking and that the concentration of these active sites increases with time-on-stream for oxidized Ga/H-MFI or upon prereduction of the catalyst in H<sub>2</sub>.

The results presented in Figure 2, together with our earlier characterization work,<sup>41</sup> suggest that [GaH]<sup>2+</sup> cations and/or [GaH<sub>2</sub>]<sup>+</sup>-H<sup>+</sup> cation pairs formed upon H<sub>2</sub> reduction of Ga/H-MFI are the active species for C<sub>3</sub>H<sub>8</sub> dehydrogenation and cracking. We propose that during the induction period observed over oxidized Ga/H-MFI, [Ga(OH)]<sup>2+</sup> cations and [Ga(OH)<sub>2</sub>]<sup>+</sup>-H<sup>+</sup> cation pairs undergo reduction to form [GaH]<sup>2+</sup> cations and [GaH<sub>2</sub>]<sup>+</sup>-H<sup>+</sup> cation pairs.

As shown in Section S.3, secondary reactions are prevalent even under conditions of differential conversion. We also show in Figure S.4 and Section 3.4 that the rates of dehydrogenation and cracking over Ga/H-MFI are inhibited by H<sub>2</sub>. To eliminate the effects of product inhibition and secondary reactions, all of the steady-state measured reaction rates reported in the balance of this study were extrapolated to zero space time (see Figure S.4).

**3.3. Effects of Ga Content on the Rates of C<sub>3</sub>H<sub>8</sub> Dehydrogenation and Cracking over Ga/H-MFI.** Figures 3a–c and 4a–c show C<sub>3</sub>H<sub>8</sub> dehydrogenation and cracking rates, measured at 733 K and 0.9 kPa C<sub>3</sub>H<sub>8</sub>/He over H-MFI and Ga/H-MFI, as functions of the Ga/Al ratio. As observed in Figure 3a, the rate of C<sub>3</sub>H<sub>8</sub> dehydrogenation (normalized per Al<sub>tot</sub> atom) increases with Ga content up to a Ga/Al ratio of 0.1 but then reaches a plateau for higher values of Ga/Al ratio. At this plateau, the rate of C<sub>3</sub>H<sub>8</sub> dehydrogenation is ~500 times higher than the corresponding rate over H-MFI, suggesting that the reactivity contribution of residual Brønsted acid O–H acid groups in Ga/H-MFI is negligible.

The rate of C<sub>3</sub>H<sub>8</sub> dehydrogenation over Ga/H-MFI can also be normalized per Ga atom by dividing the rate per Al<sub>tot</sub> by the Ga/Al<sub>tot</sub> ratio. The rate of C<sub>3</sub>H<sub>8</sub> dehydrogenation normalized this way, shown in Figure 3b, decreases monotonically as the Ga/Al ratio increases from 0.05 to 0.5, suggesting that the most active Ga species exist at the lowest Ga/Al ratios. As discussed earlier, our characterization of H<sub>2</sub>-reduced Ga/H-MFI samples used in the present study shows that for Ga/Al ≤ 0.3 the dominant Ga species present are [GaH]<sup>2+</sup> cations and [GaH<sub>2</sub>]<sup>+</sup>-H<sup>+</sup> cation pairs and that 100% of the Ga is present as [GaH]<sup>2+</sup> cations for Ga/Al = 0.1.<sup>41</sup> Moreover, the theoretical calculations supporting this work show that the formation of



**Figure 5.** (a) Dependence of the rates of C<sub>3</sub>H<sub>8</sub> dehydrogenation and (b) C<sub>3</sub>H<sub>8</sub> cracking and (c) the ratio of the rates of dehydrogenation to cracking over Ga/H-MFI (Ga/Al = 0.2) measured at 718, 733, and 753 K, on the C<sub>3</sub>H<sub>8</sub> partial pressure. In Figure 5c, triangles, circles, and diamonds indicate the ratios of rates at 718, 733, and 753 K, respectively. All rates were extrapolated to zero space time. Solid lines show regressed fits of eqs 1 and 2 to the data.

[GaH]<sup>2+</sup> cations is thermodynamically favored at NNN cation-exchange sites associated with pairs of framework Al atoms  $\leq 5$  Å apart.<sup>41</sup> Increasing the Ga/Al ratio results in the formation of [GaH<sub>2</sub>]<sup>+</sup>-H<sup>+</sup> cation pairs at NNN and NNNN cation-exchange sites associated with framework Al–Al interatomic distances  $>5$  Å apart.<sup>41</sup> Our recent theoretical calculations have shown that [GaH]<sup>2+</sup> cations are more active for C<sub>3</sub>H<sub>8</sub> dehydrogenation than [GaH<sub>2</sub>]<sup>+</sup>-H<sup>+</sup> cation pairs.<sup>36</sup> We also note in Figure 3a that the rate of dehydrogenation (per Al<sub>tot</sub>) over the Ga/Al = 0.5 sample, which contains neutral GaO<sub>x</sub> oligomeric species, in addition to cation-exchanged Ga<sup>3+</sup> species, is identical to the corresponding rate (per Al<sub>tot</sub>) over samples with lower Ga content. This suggests that neutral GaO<sub>x</sub> species are much less active for C<sub>3</sub>H<sub>8</sub> conversion in comparison to cation-exchanged Ga<sup>3+</sup> species.

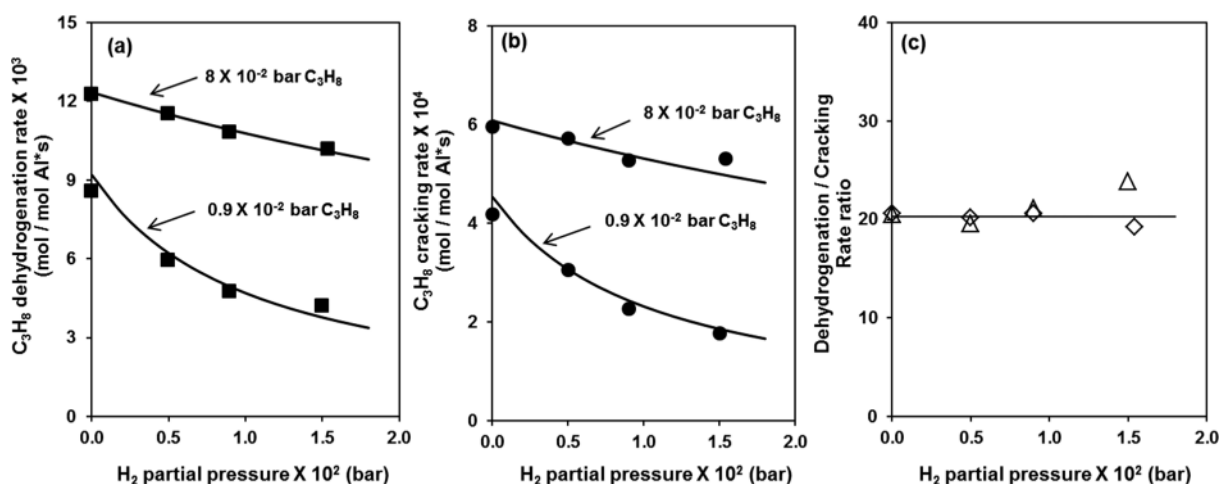
Based on the foregoing discussion, we normalize the rate of C<sub>3</sub>H<sub>8</sub> dehydrogenation by the density of [GaH]<sup>2+</sup> cations per Al<sub>tot</sub> for each Ga/Al ratio, measured via NH<sub>3</sub>-TPD (see SI S.6 for the method by which the density of [GaH]<sup>2+</sup> cations was estimated).<sup>41</sup> Figure 3c shows that the rate of C<sub>3</sub>H<sub>8</sub> dehydrogenation normalized this way is nearly independent of the Ga/Al ratio. It should be noted that the rate of C<sub>3</sub>H<sub>8</sub> dehydrogenation per [GaH]<sup>2+</sup> for the Ga/Al = 0.05 sample is about 20% higher than that for the remaining samples, which may reflect small differences between the actual fraction of [GaH]<sup>2+</sup> cations present in the Ga/Al = 0.05 sample and our estimate. We therefore conclude that the rate of C<sub>3</sub>H<sub>8</sub> dehydrogenation is approximately independent of the Ga/Al ratio. This finding supports the prediction that [GaH]<sup>2+</sup> cations are the most active species for C<sub>3</sub>H<sub>8</sub> dehydrogenation and that [GaH<sub>2</sub>]<sup>+</sup>-H<sup>+</sup> cation pairs, which constitute an increasing fraction of the Ga content in Ga/H-MFI samples with Ga/Al  $> 0.1$ , do not contribute appreciably to the measured rate.<sup>36,41</sup>

Figure 4a–c show C<sub>3</sub>H<sub>8</sub> cracking rates over H-MFI and Ga/H-MFI, also measured at 0.9 kPa C<sub>3</sub>H<sub>8</sub>/He and 733 K. Here again, measured cracking rates over Ga/H-MFI were extrapolated to zero space time. The rate of C<sub>3</sub>H<sub>8</sub> cracking normalized per Al<sub>tot</sub> atom (Figure 4a) shows a trend similar to that of the rate of C<sub>3</sub>H<sub>8</sub> dehydrogenation, increasing with Ga content up to a Ga/Al ratio of 0.1 and then reaching a plateau

for higher Ga/Al ratios. At similar conditions, the maximum rate of C<sub>3</sub>H<sub>8</sub> cracking over Ga/H-MFI (per Al<sub>tot</sub> atom) is about 20 times higher than that over H-MFI.

It is notable that an enhancement in the rate of alkane cracking over Co-, Zn-, and Ga-exchanged zeolites, relative to the corresponding H-forms of these zeolites, has been reported previously.<sup>15,37,65–67</sup> Alkane cracking over these metal-exchanged zeolites has been attributed to H<sub>2</sub>-assisted alkane hydrogenolysis catalyzed by Ga sites<sup>15,66,67</sup> or to protolytic cracking of C–C bonds by residual Brønsted acid O–H groups,<sup>33,37</sup> the acid strength of which may be enhanced by proximity to exchanged metal cations.<sup>68,69</sup> Therefore, both of these possibilities need to be considered as possible causes for the higher rate of C<sub>3</sub>H<sub>8</sub> cracking over Ga/H-MFI.

H<sub>2</sub>-assisted hydrogenolysis of C<sub>3</sub>H<sub>8</sub> would be expected to result in higher cracking rates with increasing H<sub>2</sub> concentration at higher space times (or C<sub>3</sub>H<sub>8</sub> conversion) or upon co-feeding H<sub>2</sub>. On the contrary, we find that the rate of C<sub>3</sub>H<sub>8</sub> cracking decreases with an increase in C<sub>3</sub>H<sub>8</sub> conversion and is inhibited by co-feeding H<sub>2</sub> (see Figure S.4 and Section 3.4). These results suggest that hydrogenolysis does not contribute to C<sub>3</sub>H<sub>8</sub> cracking over Ga/H-MFI. An alternative explanation is that the higher rate of C<sub>3</sub>H<sub>8</sub> cracking over Ga/H-MFI compared to H-MFI could be attributable to an increase in the acid strength of Brønsted acid O–H groups that are proximate to metal cations (here, [GaH<sub>2</sub>]<sup>+</sup> cations).<sup>68,69</sup> This phenomenon should lead to an increase in the rate of C<sub>3</sub>H<sub>8</sub> cracking with an increase in the concentration of [GaH<sub>2</sub>]<sup>+</sup>-H<sup>+</sup> cation pairs as the Ga/Al ratio increases. However, cracking rates normalized per Al<sub>tot</sub> atom do not increase with Ga content beyond a Ga/Al ratio of 0.1 (Figure 4a), while cracking rates normalized per Ga atom (Figure 4b) decrease monotonically with increasing Ga content. It is also notable that when normalized by the estimated density of [GaH]<sup>2+</sup> cations per Al<sub>tot</sub> (see SI S.6 for the method by which the density of [GaH]<sup>2+</sup> cations was estimated), the rate of C<sub>3</sub>H<sub>8</sub> cracking is independent of the Ga/Al ratio, as can be seen in Figure 4c. Taken together, these data suggest that [GaH]<sup>2+</sup> cations rather than H<sub>2</sub>-assisted hydrogenolysis by Ga sites or protolytic cracking by residual Brønsted acid O–H groups proximate to [GaH<sub>2</sub>]<sup>+</sup> cations, are responsible for the observed



**Figure 6.** Effects of  $H_2$  partial pressure on the rates of (a)  $C_3H_8$  dehydrogenation and (b)  $C_3H_8$  cracking and (c) the ratio of the rates of dehydrogenation to cracking (D/C) measured at 733 K. All rates were extrapolated to zero space time. In (c), open triangles indicate the D/C ratios measured at  $0.9 \times 10^{-2}$  bar  $C_3H_8$  and open diamonds indicate the D/C rate ratios measured at  $8 \times 10^{-2}$  bar  $C_3H_8$ . Solid lines in (a)–(c) show regressed fits of eqs 1 and 2 to the data.

**Table 1.** Values of Parameters Obtained by Nonlinear Least-Squares Regression of Eqs 1 and 2 to the Rates of  $C_3H_8$  Dehydrogenation and Cracking Measured at 733 K, Shown in Figures 5 and 6<sup>a</sup>

	$\alpha$ ( $k_{app}$ ) (mol/mol $Al_{tot}$ ·s·bar)	$\beta$ ( $K_{adsC_3}$ ) ( $bar^{-1}$ )	$\gamma$ ( $K_{adsH_2}$ ) ( $bar^{-1}$ )	$\alpha/\beta$ ( $k_{int}$ ) (mol/mol $Al_{tot}$ ·s)
dehydrogenation	3.6	$2.8 \times 10^2$	$3.3 \times 10^2$	$1.3 \times 10^{-2}$
cracking	$1.8 \times 10^{-1}$	$2.8 \times 10^2$	$3.3 \times 10^2$	$6.4 \times 10^{-4}$

<sup>a</sup>The parameters  $\beta$  and  $\gamma$  were common to both dehydrogenation and cracking in eqs 1 and 2, respectively.

enhancements in cracking rates over Ga/H-MFI. Further evidence in support of this conclusion is given below.

**3.4. Effects of  $C_3H_8$  and  $H_2$  Partial Pressures on the Rates of  $C_3H_8$  Dehydrogenation and Cracking over Ga/H-MFI.** The rates of  $C_3H_8$  dehydrogenation and cracking (per  $Al_{tot}$  atom and extrapolated to zero space time) are shown in Figure 5a and b, respectively, as functions of  $C_3H_8$  partial pressure and temperature. At all three temperatures (718, 733, 753 K), the rates of  $C_3H_8$  dehydrogenation and cracking increase monotonically with  $C_3H_8$  partial pressure at low partial pressures but become independent with respect to  $C_3H_8$  partial pressure at higher pressures. Figure 5c shows the dependence of the ratio of the rate of dehydrogenation to cracking (D/C), as a function of the  $C_3H_8$  partial pressure. For a given temperature, no discernible trend is evident in the D/C ratio as a function of  $C_3H_8$  partial pressure, suggesting that the D/C ratio is approximately independent of the surface coverage of adsorbed  $C_3H_8$ . This observed trend suggests that both dehydrogenation and cracking proceed over identical active sites in Ga/H-MFI and via a common  $C_3H_8$ -derived surface intermediate. However, the D/C ratio does exhibit a weak dependence on temperature, increasing from approximately 19.1 at 753 K to approximately 24.6 at 718 K. An increase in the value of this ratio with a decrease in temperature is consistent with the activation energy for cracking being higher than that for dehydrogenation.

As shown in Figure S4,  $H_2$  inhibits the rate of  $C_3H_8$  dehydrogenation and cracking over Ga/H-MFI. The dependence of these rates on  $H_2$  partial pressure at 733 K is shown in Figure 6a–c. While the rates of  $C_3H_8$  dehydrogenation and cracking decrease with an increase in  $H_2$  partial pressure, inhibition of these rates is more severe at lower partial pressures of  $C_3H_8$  and relatively weaker at high partial

pressures of  $C_3H_8$ . Apparent reaction orders of  $H_2$  for dehydrogenation and cracking at each  $C_3H_8$  partial pressure measured at 733 K are provided in Table S1 of the Supporting Information. These effects of  $H_2$  partial pressure are consistent with  $H_2$  competing with  $C_3H_8$  for adsorption on the active sites that catalyze both reactions. As shown in Figure 6c, the D/C ratio is independent of  $H_2$  and  $C_3H_8$  partial pressures, suggesting that  $H_2$  inhibits both dehydrogenation and cracking in a similar fashion and further supports the idea that dehydrogenation and cracking occur on the same active sites.

The observed effects of  $C_3H_8$  and  $H_2$  partial pressures on the rates of  $C_3H_8$  dehydrogenation and cracking are consistent with rate laws of the form given by eqs 1 and 2, respectively. Since the D/C ratio is nearly independent of the  $C_3H_8$  and  $H_2$  partial pressures, the denominator terms in eqs 1 and 2 are taken to be the same.

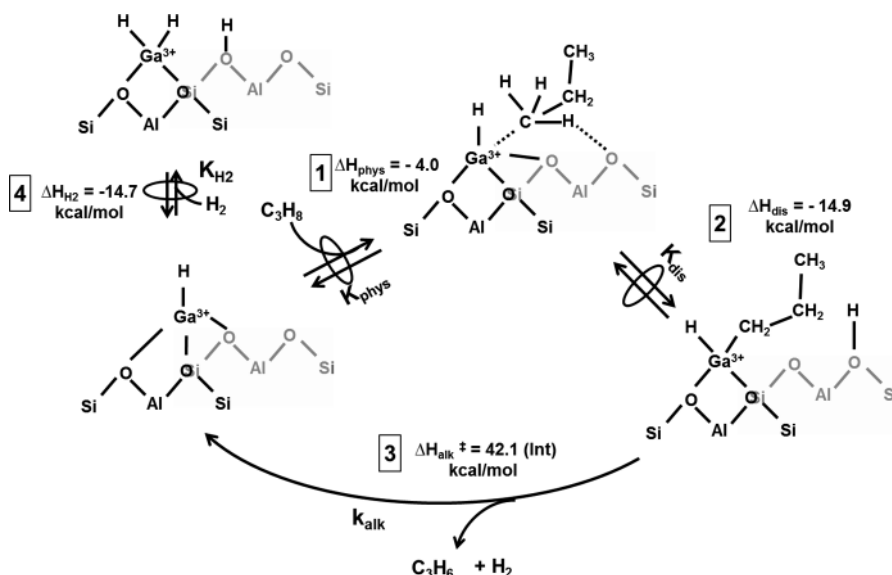
$$\frac{\text{Dehydrogenation rate}}{Al_{tot}} = \frac{\alpha_d[C_3H_8]}{1 + \beta[C_3H_8] + \gamma[H_2]} \quad (1)$$

$$\frac{\text{Cracking rate}}{Al_{tot}} = \frac{\alpha_c[C_3H_8]}{1 + \beta[C_3H_8] + \gamma[H_2]} \quad (2)$$

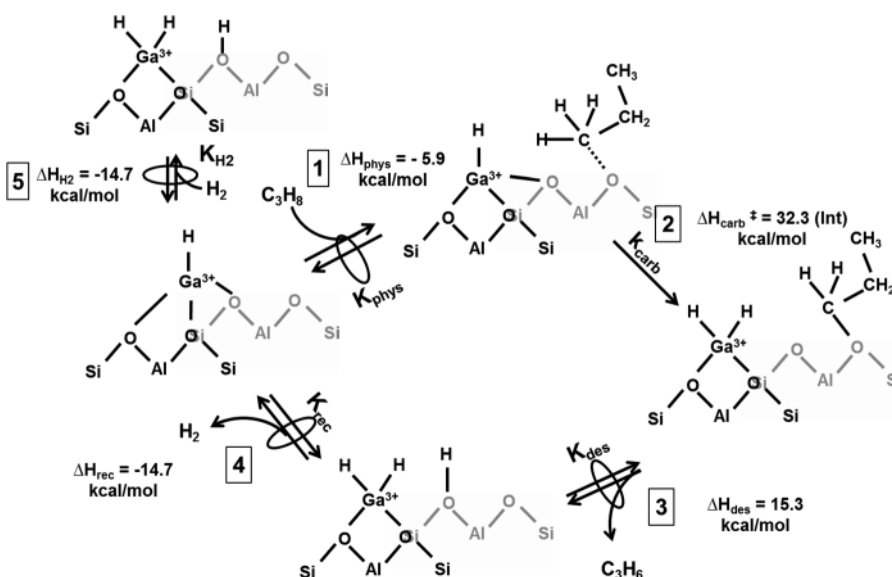
Here,  $\alpha_d$  (dehydrogenation),  $\alpha_c$  (cracking),  $\beta$ , and  $\gamma$  are parameters related to the kinetics and thermodynamics of the elementary steps involved in  $C_3H_8$  dehydrogenation and cracking.

Nonlinear regression of the data shown in Figures 5a–c and 6a–c to eqs 1 and 2, respectively, results in a satisfactory fit, represented by the solid lines in these figures. Values of  $\alpha_d$ ,  $\alpha_c$ ,  $\beta$ , and  $\gamma$  at 733 K are presented in Table 1. At very low partial pressures of  $C_3H_8$  and in the absence of co-fed  $H_2$ , eqs 1 and 2 and the data in Figures 5 and 6 indicate that the rates of dehydrogenation and cracking exhibit a first-order dependence



Scheme 1. Alkyl Mechanism for Activation and Dehydrogenation of  $C_3H_8$  over  $[GaH]^{2+}$  Sites to  $C_3H_6$  and  $H_2$ <sup>a</sup>

<sup>a</sup>Enthalpies (adsorption, reaction, and activation) for each step are shown here with respect to the enthalpy of the initial structure in the step. For each structure, framework atoms that are faded reflect cation-exchange sites that are behind the image plane for nonfaded cation-exchange sites. Cations coordinated to the faded cation-exchange sites are also behind the image plane but have not been faded for visual purposes.

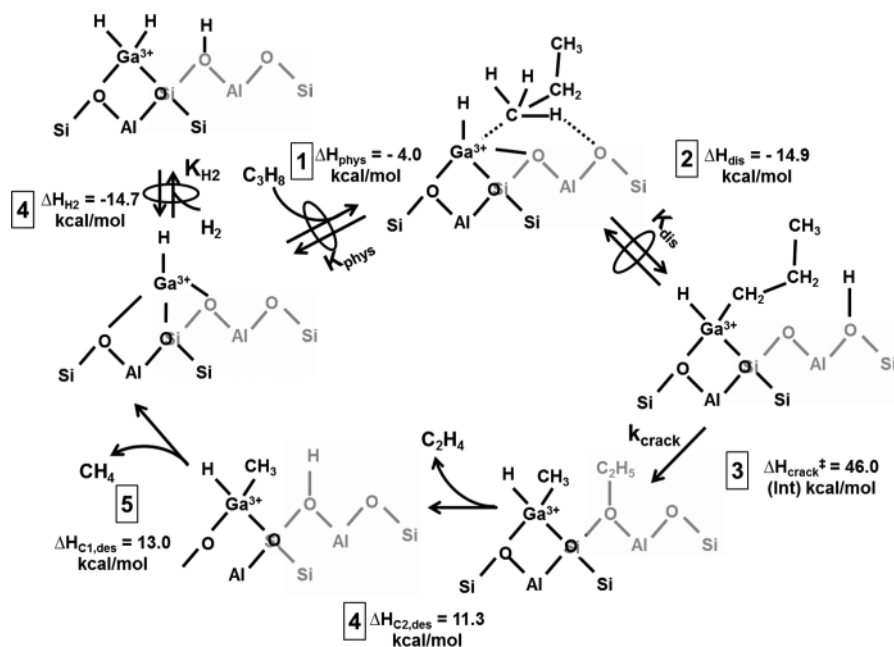
Scheme 2. Carbenium Mechanism for the Activation and Conversion of  $C_3H_8$  to  $C_3H_6$  and  $H_2$  over  $[GaH]^{2+}$  Sites<sup>a</sup>

<sup>a</sup>Enthalpies (adsorption, reaction, and activation) for each step are shown here with respect to the enthalpy of the initial structure in the step. For each structure, framework atoms that are faded reflect cation-exchange sites that are behind the image plane for nonfaded cation-exchange sites. Cations coordinated to the faded cation-exchange sites are also behind the image plane but have not been faded for visual purposes.

on  $C_3H_8$  partial pressure. The parameters  $\alpha_d$  and  $\alpha_c$  therefore reflect apparent first-order rate coefficients ( $k_{app}$ ) for dehydrogenation and cracking with units of mol/mol  $Al_{tot}$ ·s·bar. At very high partial pressures of  $C_3H_8$  and in the absence of  $H_2$ , the rates of dehydrogenation and cracking are independent of  $C_3H_8$  partial pressure, as seen from the data in Figure 5. In this case, the ratios  $\alpha_d/\beta$  and  $\alpha_c/\beta$  correspond to the zero-order rate coefficients ( $k_{int}$ ) with units of mol/mol  $Al_{tot}$ ·s. Therefore, for consistency the parameters  $\beta$  and  $\gamma$  must have units of bar<sup>-1</sup> and hence correspond to the adsorption coefficients ( $K_{ads}$ ) for  $C_3H_8$  and  $H_2$ , respectively. Further interpretation of the parameters  $\alpha$ ,  $\beta$ , and  $\gamma$  is discussed below

in the context of our examination of possible mechanisms for  $C_3H_8$  dehydrogenation and cracking over Ga/H-MFI.

**3.5. Mechanisms for  $C_3H_8$  Dehydrogenation and Cracking over  $[GaH]^{2+}$  Sites.** Based on the insight gained in Sections 3.3 and 3.4 regarding the role of  $[GaH]^{2+}$  cations in catalyzing  $C_3H_8$  dehydrogenation, we can propose two distinct mechanisms by which  $C_3H_8$  undergoes dehydrogenation over  $[GaH]^{2+}$  sites: (a) an alkyl mechanism and (b) a carbenium mechanism.<sup>36</sup> In addition, we propose an alkyl mechanism to describe the role of  $[GaH]^{2+}$  cations in the cracking of  $C_3H_8$ . The elementary steps for the alkyl and carbenium mechanisms for  $C_3H_8$  dehydrogenation and the alkyl mechanism for  $C_3H_8$

Scheme 3. Cracking of C<sub>3</sub>H<sub>8</sub> over [GaH]<sup>2+</sup> Sites by the Alkyl Mechanism<sup>a</sup>

<sup>a</sup>Enthalpies (adsorption, reaction, and activation) for each step are shown here with respect to the enthalpy of the initial structure in the step. For each structure, framework atoms that are faded reflect cation-exchange sites that are behind the image plane for nonfaded cation-exchange sites. Cations coordinated to the faded cation-exchange sites are also behind the image plane but have not been faded for visual purposes.

cracking over [GaH]<sup>2+</sup> sites are described in Schemes 1, 2, and 3, respectively. Detailed Gibbs free energy and enthalpy reaction coordinate diagrams are also provided for each of the reaction mechanisms in Figures S.6–S.9. The elementary steps presented in Schemes 1–3 can be used to derive rate equations that describe the kinetic behavior predicted by each of the mechanisms, presented here as eq 3 for alkyl-mediated dehydrogenation, eq 4 for carbenium-mediated dehydrogenation, and eq 5 for alkyl-mediated cracking. The assumptions and methods used to derive these equations are described in detail in Section S.4.

$$\frac{\text{Dehydrogenation rate}}{[\text{GaH}]^{2+}} = \frac{k_{\text{alk}}K_{\text{dis}}K_{\text{phys}}[\text{C}_3\text{H}_8]}{1 + (K_{\text{dis}}K_{\text{phys}})[\text{C}_3\text{H}_8] + K_{\text{H}_2}[\text{H}_2]} \quad (3)$$

$$\frac{\text{Dehydrogenation rate}}{[\text{GaH}]^{2+}} = \frac{k_{\text{carb}}K_{\text{phys}}[\text{C}_3\text{H}_8]}{1 + K_{\text{H}_2}[\text{H}_2]} \quad (4)$$

$$\frac{\text{Cracking rate}}{[\text{GaH}]^{2+}} = \frac{k_{\text{crack}}K_{\text{dis}}K_{\text{phys}}[\text{C}_3\text{H}_8]}{1 + (K_{\text{dis}}K_{\text{phys}})[\text{C}_3\text{H}_8] + K_{\text{H}_2}[\text{H}_2]} \quad (5)$$

In eqs 3 and 4,  $k_{\text{alk}}$  and  $k_{\text{carb}}$  are the rate coefficients for the rate-determining,  $\beta$ -hydride elimination step in the alkyl dehydrogenation sequence (step 3 in Scheme 1) and the rate-determining carbenium C–H activation step in the carbenium dehydrogenation sequence (step 2 in Scheme 2), respectively. In eq 5  $k_{\text{crack}}$  is the rate coefficient for the rate-determining C–C bond attack step in the alkyl cracking mechanism (step 3 in Scheme 3).  $K_{\text{dis}}$  is the equilibrium constant for heterolytic dissociation of C<sub>3</sub>H<sub>8</sub> to form [C<sub>3</sub>H<sub>7</sub>-GaH]<sup>+</sup>-H<sup>+</sup> cation pairs, and  $K_{\text{phys}}$  is the adsorption constant for C<sub>3</sub>H<sub>8</sub> physisorption at [GaH]<sup>2+</sup> sites.  $K_{\text{H}_2}$  is the equilibrium

constant for dissociative adsorption of H<sub>2</sub> at [GaH]<sup>2+</sup> sites to form [GaH<sub>2</sub>]<sup>+</sup>-H<sup>+</sup> cation pairs.

As seen in Schemes 1–3, alkyl-mediated pathways for dehydrogenation and cracking over [GaH]<sup>2+</sup> require dissociative adsorption of C<sub>3</sub>H<sub>8</sub> over [GaH]<sup>2+</sup> to produce [C<sub>3</sub>H<sub>7</sub>-GaH]<sup>+</sup>-H<sup>+</sup> cation pairs, prior to the rate-determining step. On the other hand, the carbenium-mediated dehydrogenation pathway proceeds via rate-determining C–H activation of C<sub>3</sub>H<sub>8</sub> species, physisorbed at [GaH]<sup>2+</sup>. In all three cases, inhibition of rates is predicted to occur via dissociative adsorption of H<sub>2</sub> at [GaH]<sup>2+</sup> to form [GaH<sub>2</sub>]<sup>+</sup>-H<sup>+</sup> cation pairs. These observations, together with an inspection of rate equations (3–5) show that only the alkyl-mediated mechanisms predict a first-order dependence of dehydrogenation and cracking rates on C<sub>3</sub>H<sub>8</sub> at low C<sub>3</sub>H<sub>8</sub> partial pressures and an inhibition of these rates by C<sub>3</sub>H<sub>8</sub> at high C<sub>3</sub>H<sub>8</sub> partial pressures via the saturation of [GaH]<sup>2+</sup> sites by strongly bound [C<sub>3</sub>H<sub>7</sub>-GaH]<sup>+</sup> species. In the carbenium mechanism, the relatively weak binding of C<sub>3</sub>H<sub>8</sub> to [GaH]<sup>2+</sup> sites, prior to the rate-determining C–H activation step, would lead to a first-order dependence of the rate of dehydrogenation on the C<sub>3</sub>H<sub>8</sub> partial pressure, in the absence of H<sub>2</sub>, as predicted by eq 4.

As seen in Figures 5 and 6, the dependence of the experimentally measured dehydrogenation and cracking rates on C<sub>3</sub>H<sub>8</sub> partial pressure is only consistent with the kinetics predicted by the alkyl-mediated mechanisms. Similarly, the D/C rate ratio in Figure 5c and Figure 6c is independent of C<sub>3</sub>H<sub>8</sub> and H<sub>2</sub> partial pressures. These observations are also consistent with the conclusion that C<sub>3</sub>H<sub>8</sub> dehydrogenation and cracking are catalyzed via a common, strongly bound C<sub>3</sub>H<sub>8</sub>-derived surface intermediate. The alkyl mechanisms for dehydrogenation and cracking also proceed via a common C<sub>3</sub>H<sub>8</sub>-derived reactive intermediate, i.e., [C<sub>3</sub>H<sub>7</sub>-GaH]<sup>+</sup>-H<sup>+</sup> cation pairs.

A further assessment of the relevant mechanisms involved in C<sub>3</sub>H<sub>8</sub> dehydrogenation and cracking over Ga/H-MFI can be

**Table 2.** Apparent and Intrinsic Activation Enthalpies for C<sub>3</sub>H<sub>8</sub> Dehydrogenation and Cracking, and Enthalpies of Dissociative Adsorption for C<sub>3</sub>H<sub>8</sub> and H<sub>2</sub>, over Ga/H-MFI (Ga/Al = 0.2), extracted from Figures S11–S13 in the SI. Also shown are Theoretically Predicted Activation Enthalpies for C<sub>3</sub>H<sub>8</sub> Dehydrogenation and Cracking over [GaH]<sup>2+</sup> Cations via Alkyl and Carbenium Mechanisms and Predicted Enthalpies of the Dissociative Adsorption of C<sub>3</sub>H<sub>8</sub> and H<sub>2</sub> over [GaH]<sup>2+</sup> Cations<sup>a</sup>

enthalpy (kcal/mol)	dehydrog. experiment <sup>b</sup>	alkyl dehydrog. mechanism <sup>c</sup>	carbenium dehydrog. mechanism <sup>c</sup>	cracking experiment <sup>b</sup>	alkyl cracking mechanism <sup>c</sup>
$\Delta H_{app}^{\ddagger}$	19.0 ± 6.0	23.2	26.4	26.5 ± 0.3	27.1
$\Delta H_{int}^{\ddagger}$	34.6 ± 1.0	42.1	32.3	42.0 ± 4.7	46.0
$\Delta H_{ads}(C_3H_8)$	-15.6 ± 5.0	-18.9	-5.9	-15.6 ± 5.0	-18.9
$\Delta H_{ads}(H_2)$	-7.4 ± 3.3	-14.6	-14.6	-7.4 ± 3.3	-14.6

<sup>a</sup>Reported uncertainties reflect 95% confidence intervals. <sup>b</sup>Obtained from fits of first- and zero-order rate coefficients ( $k_{app}$  and  $k_{int}$ ), measured at 718 K, 733 K and 753 K over the Ga/Al = 0.2 sample, to eqs S24, S25, and S26.<sup>41</sup> <sup>c</sup>Computed using QM/MM methods. See theoretical methods section for more details.

obtained by comparing experimentally derived activation and adsorption enthalpies to their values predicted theoretically. Experimental activation and adsorption enthalpies were obtained by measuring the rates of C<sub>3</sub>H<sub>8</sub> dehydrogenation and cracking at different temperatures (718–753 K) over the Ga/Al = 0.2 sample and then determining values of the apparent and intrinsic activation enthalpies for both reactions. The methods used for extracting values of these parameters from kinetic data are provided in Section S.5, and plots showing the temperature dependence of rate coefficients and adsorption coefficients are provided in Figures S.10–S.12.

Experimental values of the activation and adsorption enthalpies for C<sub>3</sub>H<sub>8</sub> dehydrogenation and cracking over Ga/H-MFI (Ga/Al = 0.2) are given in Table 2. Also shown in this table are the apparent and intrinsic activation and adsorption enthalpies predicted from QM/MM calculations for the alkyl and carbenium mechanisms for C<sub>3</sub>H<sub>8</sub> dehydrogenation and for the alkyl mechanism for C<sub>3</sub>H<sub>8</sub> cracking, in all three cases over [GaH]<sup>2+</sup> sites. For C<sub>3</sub>H<sub>8</sub> dehydrogenation, the experimentally measured apparent activation enthalpy is 19.0 ± 6.0 kcal/mol and the intrinsic activation enthalpy is 34.6 ± 1.0 kcal/mol, whereas the adsorption enthalpy for C<sub>3</sub>H<sub>8</sub> extracted from experimental data is -15.6 ± 5.0 kcal/mol. These estimates of the C<sub>3</sub>H<sub>8</sub> adsorption enthalpy and the apparent and intrinsic enthalpies are consistent with theoretical predictions for the formation of [C<sub>3</sub>H<sub>7</sub>-GaH]<sup>+</sup>-H<sup>+</sup> cation pairs upon dissociative C<sub>3</sub>H<sub>8</sub> adsorption at [GaH]<sup>2+</sup> sites (-18.9 kcal/mol) and  $\beta$ -hydride elimination of C<sub>3</sub>H<sub>6</sub> and H<sub>2</sub> (predicted  $\Delta H_{app} = 23.2$  kcal/mol and predicted  $\Delta H_{int} = 42.1$  kcal/mol). As noted earlier, the carbenium mechanism involves the activation of an adsorbed C<sub>3</sub>H<sub>8</sub> precursor that is weakly bound to the active site, leading to smaller differences between the apparent and intrinsic activation enthalpies than those measured experimentally and to a rate expression for C<sub>3</sub>H<sub>8</sub> dehydrogenation that is inconsistent with that observed experimentally (compare eq 1 with eqs 3 and 4).

The DFT-predicted value for the dissociative adsorption of C<sub>3</sub>H<sub>8</sub> on [GaH]<sup>2+</sup> is more exothermic than that for dissociative adsorption of H<sub>2</sub>, a finding that is consistent with the experimentally measured adsorption enthalpies reported in Table 2. However, the value for the predicted adsorption enthalpy of H<sub>2</sub> at [GaH]<sup>2+</sup> sites is lower than that deduced from the analysis of the reaction kinetics. A part of this discrepancy may be due to the sensitivity of the predicted value to the interatomic distance between framework Al atoms involved in proximate cation-exchange sites that host [GaH]<sup>2+</sup> cations.<sup>35,36</sup> For the NNN Al atom configurations considered, the predicted enthalpy for dissociative adsorption of H<sub>2</sub> over

[GaH]<sup>2+</sup> cations to form [GaH<sub>2</sub>]<sup>+</sup>-H<sup>+</sup> cation pairs varies between -5.5 and -15.9 kcal/mol. This range encompasses the experimental H<sub>2</sub> adsorption enthalpy value of -7.4 ± 3.3 kcal/mol shown in Table 2.

Table 2 also shows apparent and intrinsic activation enthalpies for C<sub>3</sub>H<sub>8</sub> cracking via the alkyl mechanism over [GaH]<sup>2+</sup> predicted from theoretical calculations. The experimentally measured apparent activation enthalpy (26.5 ± 0.3 kcal/mol) is in excellent agreement with the theoretically predicted estimate (27.1 kcal/mol). The experimentally measured intrinsic activation enthalpy, 42 ± 4.7 kcal/mol, is also in good agreement with the theoretical estimate (44.9 kcal/mol).

The data presented in Table 2 further support the hypothesis that both dehydrogenation and cracking of C<sub>3</sub>H<sub>8</sub> over Ga/H-MFI are catalyzed by [GaH]<sup>2+</sup> sites via a common alkyl-Ga, [C<sub>3</sub>H<sub>7</sub>-GaH]<sup>+</sup> surface intermediate. Inhibition of both rates occurs by dissociative adsorption of H<sub>2</sub> at [GaH]<sup>2+</sup> to form [GaH<sub>2</sub>]<sup>+</sup>-H<sup>+</sup> cation pairs. Consistent with this interpretation, the D/C ratio, shown in Figure 5c and Figure 6c, is independent of C<sub>3</sub>H<sub>8</sub> and H<sub>2</sub> surface coverage, but weakly dependent on temperature. Therefore, the selectivity to C<sub>3</sub>H<sub>8</sub> dehydrogenation versus cracking over Ga/H-MFI is not governed by the concentrations of C<sub>3</sub>H<sub>8</sub>, H<sub>2</sub>, or residual Brønsted acid O-H groups in Ga/H-MFI, but rather by the difference between the free energy activation barriers for dehydrogenation and cracking over [GaH]<sup>2+</sup>. A higher activation enthalpy for cracking than for dehydrogenation would lead to a decrease in the D/C ratio with an increase in temperature, as observed experimentally in Figure 5c. Indeed, Table 2 indicates that the difference in the measured activation enthalpies (apparent or intrinsic) between cracking and dehydrogenation over Ga/H-MFI,  $\Delta\Delta H_{C/D}^{\ddagger}(\text{exp})$ , is 7.4 ± 4.8 kcal/mol. Consistent with this finding, our theoretical calculations predict a higher activation enthalpy for alkyl-mediated cracking than for alkyl-mediated dehydrogenation ( $\Delta\Delta H_{C/D}^{\ddagger}(\text{calc}) = 3.9$  kcal/mol).

We turn next to a comparison of our results with those recently reported by Schreiber et al.<sup>37</sup> Ga/H-MFI samples (Si/Al = 50) in their work were prepared using conventional incipient wetness impregnation followed by H<sub>2</sub> reduction. Both C<sub>3</sub>H<sub>8</sub> dehydrogenation and cracking rates were shown to increase with Ga content up to a Ga/Al ratio of 0.5, with further increases in Ga content leading to lower rates of dehydrogenation and cracking. Similar to our findings, the rate of C<sub>3</sub>H<sub>8</sub> dehydrogenation was shown to exhibit a Langmuir–Hinshelwood dependence on C<sub>3</sub>H<sub>8</sub> partial pressure, but the

dependence of the rate of dehydrogenation on  $H_2$  partial pressure was not investigated.

Schreiber et al. have proposed that  $Ga^+-H^+$  cation pairs are responsible for the dehydrogenation of  $C_3H_8$ . This conclusion is based on the observation of a peak at 10 370.2 eV in the XANES spectrum of their sample of  $H_2$ -reduced Ga/H-MFI, attributed to  $Ga^+$  cations and to the observation that the rate of dehydrogenation increases with Ga content up to a Ga/Al ratio of 0.5.<sup>37</sup> Periodic DFT calculations were then employed to show how  $Ga^+-H^+$  cation pairs residing at proximate cation-exchange sites associated with NNN pairs of framework Al atoms could catalyze  $C_3H_8$  dehydrogenation. In this scheme, the  $Ga^+-H^+$  cation pair is first converted into a  $[GaH]^{2+}$  cation via oxidative addition, and the latter species is assumed to catalyze the alkyl C–H activation of  $C_3H_8$  to form a  $[C_3H_7-GaH]^+-H^+$  cation pair. This step is then followed by a monomolecular elimination of  $H_2$  from the  $[C_3H_7-GaH]^+-H^+$  cation pair and subsequent release of  $C_3H_6$  to regenerate  $Ga^+-H^+$  cation pair sites. Both alkyl C–H activation and  $H_2$  elimination steps were reported to be kinetically relevant.

We have examined several aspects of the mechanism proposed by Schieber et al.<sup>37</sup> The first is the ability of  $[GaH]^{2+}$  cations to undergo reductive elimination to form  $Ga^+-H^+$  cation pairs. We find that the Gibbs free energy for this reaction is  $-10.4$  kcal/mol and that the free energy barrier for the reductive elimination of  $H^+$  from  $[GaH]^{2+}$  to form  $Ga^+-H^+$  cation pairs is 25.2 kcal/mol. This indicates that the formation of  $Ga^+-H^+$  cation pairs from  $[GaH]^{2+}$  cations is both thermodynamically and kinetically feasible (see Figure S.8). However, the free energy (77.8 kcal/mol) and enthalpy (26.3 kcal/mol) activation barriers for the C–H activation step via the mechanism reported by Scheiber et al. on the given  $[GaH]^{2+}$  site are considerably higher than the corresponding values reported in Scheme 1 and in Figure S7, 40.1 and 2.0 kcal/mol, respectively. We believe that the difference in the energetics reported here and by Scheiber et al.<sup>37</sup> is a consequence of how  $[GaH]^{2+}$  cations are coordinated with the zeolite framework. In the latter study,  $[GaH]^{2+}$  cations are bound to two framework O atoms, whereas in our work,  $[GaH]^{2+}$  cations are bound to three framework O atoms (and one H ligand), thus forming the preferred tetrahedral coordination around the  $Ga^{3+}$  center.<sup>70</sup> The three framework O atoms in the first coordination sphere of these species withdraw more electron density from the  $Ga^{3+}$  center, resulting in  $[GaH]^{2+}$  cations that are more Lewis acidic and therefore more reactive toward alkane C–H activation than  $[GaH]^{2+}$  cations that are bound to only two framework O atoms.

We have also investigated the free energy landscape for the dehydrogenation pathway over  $Ga^+-H^+$  cation pairs proposed by Schreiber et al. Our calculations indicate that the rate-determining step for this sequence is the concerted elimination of  $C_3H_6$  and  $H_2$  from  $[C_3H_7-GaH]^+-H^+$  cation pairs to re-form  $Ga^+-H^+$  cation pairs (see Figure S8). The Gibbs free energy barrier for this rate-determining transition state is about 20 kcal/mol higher than that for the rate-determining step in the alkyl sequence over  $[GaH]^{2+}$  shown in Scheme 1 (see Figure S7), thereby rendering the former pathway less favorable. Thus, while our theoretical calculations predict that the formation of  $Ga^+-H^+$  cation pairs from  $[GaH]^{2+}$  cations is thermodynamically and kinetically feasible, these calculations also predict that the dehydrogenation of  $C_3H_8$  via processes involving  $Ga^+-H^+$  cation pairs would be much less favorable than those involving  $[GaH]^{2+}$  cations. We also show that while

$Ga^+-H^+$  cation pairs can activate  $C_3H_8$  to produce  $[C_3H_7-GaH]^+-H^+$  cation pairs, the barrier to form  $[GaH]^{2+}$  cations from  $[C_3H_7-GaH]^+-H^+$  cation pairs is much lower than that to regenerate  $Ga^+-H^+$  cation pairs (see Figure S15). Therefore, our findings strongly suggest that  $[GaH]^{2+}$  cations are the primary active sites responsible for dehydrogenation.

#### 4. CONCLUSIONS

The kinetics of  $C_3H_8$  dehydrogenation and cracking were investigated over Ga/H-MFI, prepared with Ga/Al ratios between 0.05 and 0.3, for which all of the Ga is presented as isolated cationic species.  $C_3H_8$  conversion occurs over H-MFI via monomolecular dehydrogenation and cracking catalyzed by Brønsted O–H acid groups.  $C_3H_8$  conversion over preoxidized Ga/H-MFI undergoes an induction period before reaching a steady-state activity. The induction period is significantly attenuated by prereducing the catalysts in  $H_2$ . Notably, the distribution of products formed via  $C_3H_8$  dehydrogenation and cracking is virtually unchanged during the induction period, and the steady-state activities of Ga/H-MFI are independent of the initial state of cationic  $Ga^{3+}$  species (oxidized or reduced). Reaction rates (expressed per  $Al_{tot}$  atom) for  $C_3H_8$  dehydrogenation and cracking over Ga/H-MFI (Ga/Al = 0.2) are  $\sim 500$  and  $\sim 20$  times, respectively, higher than the corresponding rates over H-MFI at identical conditions. Rates of both reactions when normalized with respect to the concentration of  $[GaH]^{2+}$  cations are found to be independent of the Ga/Al ratio, suggesting that  $[GaH]^{2+}$  cations are the catalytically active centers for both reactions.  $C_3H_8$  dehydrogenation and cracking rates over Ga/H-MFI are first-order in  $C_3H_8$  at low  $C_3H_8$  partial pressures and are inhibited by  $C_3H_8$  at higher  $C_3H_8$  partial pressures. Both reactions are inhibited by the presence of  $H_2$ . Ratios of the rates of dehydrogenation to cracking (D/C) are, however, independent of the partial pressures of  $C_3H_8$  and  $H_2$  and only dependent upon temperature, again suggesting that both reactions involve the same active center. The observed dependences of reaction rates on the partial pressures of  $C_3H_8$  and  $H_2$  as well as both the apparent and intrinsic activation enthalpies are consistent with theoretical predictions based on a proposed alkyl-mediated mechanism for the two reactions. The alkyl-mediated mechanism for  $C_3H_8$  dehydrogenation and cracking begins with the reversible, dissociative adsorption of  $C_3H_8$  at  $[GaH]^{2+}$  to form  $[C_3H_7-GaH]^+-H^+$  cation pairs. Dehydrogenation then proceeds via rate-determining  $\beta$ -hydride elimination from the  $C_3H_7$  fragment to form  $C_3H_6$  and  $H_2$  in a concerted step involving a cyclic transition state. On the other hand, cracking proceeds via rate-determining C–C bond attack of the  $C_3H_7$  fragment by the proximal Brønsted acid O–H group, resulting in the formation of  $[CH_3-GaH]^+$  cations proximal to ethoxide species.  $C_2H_4$  and  $CH_4$  are then formed in subsequent steps that are not kinetically relevant. Inhibition of both dehydrogenation and cracking by  $H_2$  occurs via dissociative adsorption of  $H_2$  at  $[GaH]^{2+}$  cations to produce  $[GaH_2]^+-H^+$  cation pairs, which are much less active for  $C_3H_8$  dehydrogenation and cracking.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.8b11443.



Details regarding characterization, catalytic rate measurements, and theoretical calculations ([PDF](#))

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### Notes

The authors declare no competing financial interest.

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