First Principles Analysis of Ethylene Oligomerization on Single-site Ga$^{3+}$ Catalysts Supported on Amorphous Silica

Supporting Information

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(S.1) Ga$^{3+}$ site creation and formation energies

Each Ga$^{3+}$ site was created by replacing an Si atom with Ga. A proton was added to the adjacent oxygen atom to maintain charge balance. Five Si atoms were tested and replaced, with four possible oxygen atoms per site, yielding a total of 20 distinct Ga site configurations (Figure S1).

Figure S1. Top view of unit cell used for the amorphous silica model, with locations indicated for the Si atoms used for creating Ga sites.
Table S1. Ga-hydroxyl distance of the 20 tested Ga-substituted configurations, together with the corresponding Si-O bond lengths of the original Si atoms

| Site index | 1   | 2   | 3   | 4 (3CN) |
|------------|-----|-----|-----|---------|
| Ga-hydroxyl distance, Å | 2.98 | 3.58 | 4.06 | 4.57    |
| Site index | 5   | 6   | 7   | 8 (4CN) |
| Ga-hydroxyl distance, Å | 2.9  | 2.14 | 2.16 | 2.02    |
| Site index | 9   | 10  | 11  | 12      |
| Ga-hydroxyl distance, Å | 2.16 | 2.36 | 2.16 | 2.18    |
| Site index | 13  | 14  | 15  | 16      |
| Ga-hydroxyl distance, Å | 4.22 | 2.67 | 4.80 | 4.22    |
| Site index | 17  | 18  | 19  | 20      |
| Ga-hydroxyl distance, Å | 2.14 | 2.50 | 2.70 | 2.09    |

| Si atom index | 1 |
| Si-O bond length, Å | 1.66 | 1.69 | 1.75 | 1.80 |
| Si atom index | 2 |
| Si-O bond length, Å | 1.67 | 1.64 | 1.66 | 1.62 |
| Si atom index | 3 |
| Si-O bond length, Å | 1.65 | 1.67 | 1.64 | 1.66 |
| Si atom index | 4 |
| Si-O bond length, Å | 1.74 | 1.70 | 1.73 | 1.70 |
| Si atom index | 5 |
| Si-O bond length, Å | 1.65 | 1.68 | 1.67 | 1.66 |
Table S2. Free energies of proton transfer, $\beta$-hydride elimination, and ethylene-assisted $\beta$-hydride elimination pathways on 3CN and 4CN Ga sites ($T = 523$ K). The adsorption energies are referenced to empty Ga sites and appropriate amounts of gaseous ethylene molecules at 1 atm.

| species number | 1 | †1 | 2 | 3 | †2 | 4 |
|----------------|---|----|---|---|----|---|
| description    | Ga(III) | TS | Ga-vinyl | Ga-vinyl, physisorbed ethylene | TS | Ga-butanyl |
| free energy (3CN), eV | 0 | 0.93 | -0.97 | -1.21 | 0.26 | -1.26 |
| free energy (4CN), eV | 0 | 1.19 | 0.14 | 1.40 | 2.64 | -0.21 |
| entropy (3CN), kJ mol$^{-1}$ | 98.7 | 232.6 | 232.6 | 332.7 | 332.7 | 287.2 |
| entropy (4CN), kJ mol$^{-1}$ | 66.8 | 238.2 | 238.2 | 312.6 | 312.6 | 322.0 |

| species number | †a | 5a | †b | 5b | 6b |
|----------------|---|----|----|---|---|
| description    | TS | Ga(III) | TS | Ga-hydride, physisorbed n-butene | Ga-hydride |
| free energy (3CN), eV | 1.42 | -0.11 | 0.87 | -0.70 | -0.97 |
| free energy (4CN), eV | 0.90 | -0.11 | 2.20 | 0.41 | 0.50 |
| entropy (3CN), kJ mol$^{-1}$ | 287.2 | 98.7 | 287.2 | 359.0 | 124.1 |
| entropy (4CN), kJ mol$^{-1}$ | 322.0 | 66.8 | 322.0 | 348.6 | 134.3 |

| species number | 5c | †c | 6c | 7c |
|----------------|---|----|---|---|
| description    | Ga-butenyl, physisorbed ethylene | TS | Ga-ethyl, physisorbed butadiene | Ga-ethyl |
| free energy (3CN), eV | -1.60 | -0.80 | -1.93 | -1.72 |
| free energy (4CN), eV | 1.12 | 1.48 | -0.62 | -0.26 |
| entropy (3CN), kJ mol$^{-1}$ | 478.0 | 477.9 | 477.9 | 253.7 |
| entropy (4CN), kJ mol$^{-1}$ | 409.4 | 433.2 | 457.0 | 247.8 |
(S.3) Dehydration of constrained Ga sites

For a 4CN Ga site, a Si-OH moiety is close to the Ga site due to the constrained environment. The activation of a C-H bond of ethylene on these sites then generates a second Si-OH moiety. The proximity of the two Si-OH groups can lead to a dehydration step, which results in an oxygen bridged Si pair and a water molecule. Figure S2 shows the pathways after the dehydration step, and Figure S3 shows the schematics of the dehydration step of a 4CN site. With the absence of the Si-OH moiety, the proton transfer step, which reforms the original 4CN Ga site, is not possible. Two other pathways, including β-hydride elimination and β-hydride transfer, are also examined. Figure S5 shows the free energy landscape of the dehydrated 4CN Ga site, demonstrating that the β-hydride transfer pathway is more energetically favorable.

Figure S2. Two site activation pathways after a dehydration step of a constrained 4CN Ga site.
Figure S3. Site activation pathways after a dehydration step on a constrained 4CN Ga site. The two adjacent Si-OH groups are represented by H₁ and H₂.

Figure S4. Free energy diagram of the 4CN site dehydration, followed by the \( \beta \)-hydride elimination and \( \beta \)-hydride transfer pathways (T = 523 K). The adsorption energies are referenced to empty site and appropriate amounts of gaseous ethylene molecules at 1 atm.
Table S3. Energy information of ethylene oligomerization (T = 523 K), the adsorption energies are referenced to Ga-ethyl species and appropriate amounts of gaseous ethylene molecules at 1 atm.

| species number | 1-1       | 1-2       | ‡       | 1-3       | ‡b      | 0-4       |
|----------------|-----------|-----------|---------|-----------|---------|-----------|
| description    | Ga-ethyl  | Ga-ethyl, | TS      | Ga-n-butyl| TS      | Ga-hydride,|
|                |           | physisorbed|         |           |         | physisorbed|
|                |           | ethylene   |         |           |         | ethylene  |
| free energy    | 0         | -0.31     | 1.37    | -0.47     | 1.96    | 0.34      |
| (3CN), eV      |           |           |         |           |         |           |
| Entropy, kJ     | 253.7     | 419.1     | 419.1   | 378.0     | 378.0   | 362.8     |
| mol⁻¹           |           |           |         |           |         |           |

| species number | 0-5       | 1-4       | ‡a      | 1-5       |
|----------------|-----------|-----------|---------|-----------|
| description    | Ga-hydride| Ga-n-butyl|TS      | Ga-ethyl, |
|                |           | physisorbed|        | physisorbed|
|                |           | ethylene   |        | n-butene  |
| free energy    | 0.67      | -0.24     | 0.80    | -0.07     |
| (3CN), eV      |           |           |         |           |
| Entropy, kJ     | 124.3     | 454.9     | 454.9   | 465.3     |
| mol⁻¹           |           |           |         |           |
(S.5) Free energy landscapes of Ga-hydride-centered Cossee-Arlman mechanism on 3CN and 4CN sites

Figure S5. Top and side views of key intermediates and transition states of ethylene oligomerization on Ga-H generated from a post-dehydrated 4CN Ga (Si = blue, O = red, H= white, Ga = green)

Figure S6. Top and side views of key intermediates and transition states of ethylene oligomerization on Ga-H generated from 4CN Ga (Si = blue, O = red, H= white, Ga = green)

Figure S7. Top and side views of key intermediates and transition states of ethylene oligomerization on a Ga-H moiety located in a less constrained, 3CN environment (Si = blue, O = red, H= white, Ga = green)
Figure S8. Free energy landscapes ($T = 523$ K) of ethylene oligomerization on three types of Ga-H sites: Ga-H formed without (orange, solid) and with (orange, dashed) dehydration on the 4CN Ga site, and Ga-H formed using the less constrained 3CN Ga site (black, solid). The adsorption energies are referenced to Ga-hydride species and appropriate amounts of gaseous ethylene molecules at 1 atm.
(S.6) Complete list of elementary steps in microkinetic model of ethylene oligomerization.

Figure S9. Elementary reactions used in microkinetic modeling

1. $^* + A \leftrightarrow A^*$
2. $A^* \leftrightarrow B^*$
3. $B^* + A \leftrightarrow C^*$
4. $C^* \leftrightarrow D^*$
5. $D^* \leftrightarrow ^* + D$
(S.7) Construction of microkinetic model

Adsorption of gas molecules are described using collision theory. The rate constant of this process is represented by:

\[ k_{ads} = \frac{A_0 \Lambda}{(2\pi kT)^2} \]

where \( A_0 \) is the area of the surface site, and \( \Lambda \) is the probability of adsorbate sticking, which is assumed to be one.

The forward rate constant of a surface reaction is calculated using the following equation:

\[ k_{rx,f} = \frac{kT}{h} e^{-\frac{(G_{TS}-G)}{kT}} \]

It can be noticed that transition state theory is employed to incorporate the free energy of the transition state. The potential energy, ZPE, and entropy effects have been included in the free energy.

The equilibrium constants for each elementary step are defined by:

\[ K_{eq} = e^{\frac{(G_{prod}-G_{react})}{kT}} \]

For surface reactions, the reverse rate constant can be obtained by:

\[ K_{eq} = \frac{k_{rx,f}}{k_{rx,r}} \]

In a differential reactor with a low conversion, the equation that describes the mass balance of each gaseous species is:

\[ \frac{dF}{dt} = F_{in} - F - b(rate) \]

where term \( b \) is related to site normalization. To obtain a reaction rate comparable to the experiments, the rates are normalized by the number of Ga sites in the catalyst.

The differential equation that describes the mass of each surface species (using \( A^* \) as an example) is:

\[ \frac{d\Theta_{A^*}}{dt} = rate \]

The differential equations, together with the site balance equation, are solved in MATLAB until steady state is reached.
(S.8) Calculation of entropy using mode decompositions

Harmonic vibrational modes form the basis for calculating most adsorbate entropies. However, for vibrational modes with low wavenumbers (< 150 cm\(^{-1}\)), particle-in-a-box (PIB) and free rotor schemes are used for calculating their entropic contributions. For a low frequency that corresponds to translation of a molecule, the PIB model is used with a length scale corresponding to the size of the cavity where the Ga site is located; the theoretical treatment produces a lower entropy limit of the vibrational mode. On the other hand, for a low frequency vibration that resembles rotation of a molecule, the free rotor model is used and likely represents a small overestimate of the corresponding entropy. Finally, the entropies of the transition states are approximated as being equivalent to the entropies of the corresponding reactants or products, depending on whether the geometry of the transition state more closely resembles that of reactants or products.

Table S4 outlines examples of entropy calculations for Ga-n-butyl and Ga-ethyl intermediates.

Table S4. Examples of entropy contributions from the vibrational modes with wavenumbers less than 150 cm\(^{-1}\) (T = 250 °C)

| Wavenumber, cm\(^{-1}\) | Description | Entropy contribution, J mol\(^{-1}\) K\(^{-1}\) | Wavenumber, cm\(^{-1}\) | Description | Entropy contribution, J mol\(^{-1}\) K\(^{-1}\) |
|-------------------------|-------------|---------------------------------|-------------------------|-------------|---------------------------------|
| 64.4                    | Translation (adsorbate + Ga) | 40.5                           | 23.5                    | Translation | 38.2                           |
| 70.1                    | Ga vibration | 33.0                           | 46.8                    | Ga vibration | 33.0                           |
| 101.4                   | Rotation     | 25.6                           | 63.3                    | Translation | 38.2                           |
| 137.4                   | Ga vibration | 33.0                           | 81.9                    | Rotation     | 34.2                           |
| 152.5                   | Rotation     | 25.6                           | 120.0                   | Ga vibration | 33.0                           |
|                         |             |                                | 127.3                   | Translation (adsorbate + Ga) | 41.5                           |
|                         |             |                                | 137.4                   | Rotation     | 34.2                           |
Derivation of simplified kinetic equation

(1)  $A + \ast \rightleftharpoons A^\ast$

(2)  $A^\ast \rightarrow B^\ast$

(3)  $A + B^\ast \rightleftharpoons D + \ast$

Assumptions motivated by the microkinetic modeling results are: (1) Steps 1 and 3 are quasi-equilibrated; (2) Step 2 is irreversible and rate-determining, and (3) the coverage of empty sites is negligible.

The overall reaction rate per Ga site is:

$$\frac{r_{\text{overall}}}{N} = k_2 \theta_A$$

where $r_{\text{overall}}$ is the rate per unit surface area, $N$ denotes the total number of reactive Ga sites, and $\theta_A$ denotes the fractional coverage of species A (ethylene physisorbed on Ga-ethyl). If we apply the assumptions on the other steps, we have:

$$\theta_A = K_1 P_A \theta_s$$
$$\theta_B = K_3 \frac{P_D}{P_A} \theta_s$$

where $P$ is the gas-phase partial pressure, and $\theta_s$ is the coverage of empty sites. We can write the total balance of sites as:

$$1 = \theta_s + \theta_A + \theta_B$$

Therefore:

$$\frac{r_{\text{overall}}}{N} = \frac{k_2 K_1 P_A}{\left( 1 + K_1 P_A + K_3 \frac{P_D}{P_A} \right)}$$
(S.10) Arrhenius plot at 523 K, 1 atm, and pure ethylene feed

From the Arrhenius plot, where the temperature was varied, an apparent activation barrier of 1.52 eV is obtained. This corresponds well to the value obtained from the free energy analysis.

Figure S10. Arrhenius plot at 523 K, 1 atm, and pure ethylene feed on a 3CN Ga site