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Density functional theory and microkinetics of ethylene chain growth and termination on silica grafted group 4 metal hydrides

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Abstract

The creation and ethylene oligomerization function of silica-anchored group 4 metal (M = Ti, Zr, Hf) hydrides as a function of anchor site structure are explored using density functional theory models. Oligomerization potential energy surfaces are sensitive both to metal ion and to the structure of the anchoring site. Microkinetic models predict oligomerization rate and degree of polymerization as a function of site, temperature, and reactant pressures. Intrinsic catalytic activity is predicted to vary as Ti < Zr > Hf down the group, irrespective of site model, while absolute rates and product distributions are strongly sensitive to site model, temperature, and hydrogen pressure. Catalysts based on these sites are plausible candidates for high-temperature ethylene oligomerization of interest for generating fuels from ethylene, but selectivity is expected to require careful control over site structure and reaction conditions.

Keywords

Silica, single-site catalyst, metal hydride, ethylene oligomerization, density functional theory
1 Introduction

Group 4 metal (M = Ti, Zr, Hf) ions anchored to oxide supports are known to catalyze a wide variety of hydrocarbon transformations.\(^1\)\(^-\)\(^4\) Initially explored as heterogeneous catalysts for olefin polymerization,\(^5\)\(^-\)\(^6\) anchored heterogenized ions have also been shown to activate paraffinic C–H bonds and to depolymerize paraffins.\(^7\)\(^-\)\(^12\) Zakharov et al. demonstrated early on that group 4 tetraalkyl precursors dosed to silica and treated with hydrogen form catalysts active for ethylene polymerization at near ambient temperatures,\(^5\)\(^-\)\(^6\)\(^,\)\(^11\) as evidenced by the appearance of vibrational features characteristic of methylene and methyl groups.\(^1\)\(^,\)\(^5\)\(^,\)\(^6\)

Depolymerization and hydrogenolysis is observed when the polymer/catalyst combination is treated in hydrogen at elevated temperature.\(^1\)\(^,\)\(^13\) Similarly prepared Ti,\(^7\)\(^,\)\(^14\) Zr,\(^8\)\(^,\)\(^9\)\(^,\)\(^11\)\(^,\)\(^12\) and Hf\(^1\)\(^,\)\(^10\) catalysts are also observed to be active for hydrogenolysis of waxes and alkanes at 150 – 180°C. These observations reflect the ability of anchored group 4 ions to form, rearrange and cleave C–C bonds, and thus their potential utility as oligomerization catalysts at elevated temperatures.

Controlled coupling of ethylene into short-chain linear alpha olefins (LAOs) or transportation fuels is particularly timely and relevant.\(^15\) The development of shale gas reserves has created a rich new source of light hydrocarbons, including ethane.\(^16\) Ridha et al. have shown that catalytic dehydrogenation of ethane to ethylene followed by oligomerization is a potentially efficient route to liquid fuel.\(^17\) A hydrogen-tolerant, high temperature, and selective oligomerization catalyst would obviate the need for hydrogen separation before oligomerization. In this light, hydrogen treated, supported group-4 metal catalysts are appealing candidates as potential oligomerization catalysts. As evidence of the potential, Szeto et al. have reported that anchored Zr is highly selective for 2-butene dimerization at elevated pressure and temperature.\(^18\)

The generation of anchored single-site catalysts typically takes advantage of the reaction of metal alkyl precursors with surface hydroxyls.\(^2\)\(^,\)\(^19\) The precise nature of the resultant site
is observed to be a function of the hydroxyl coverage. Active catalysts are prepared by treatment in hydrogen to remove residual alkyls and form surface hydrides. These processes have been followed spectroscopically using vibrational (IR), $^1$H/$^{29}$Si and $^1$H/$^{13}$C solid state nuclear magnetic resonance (NMR) and $^1$H DQ solid-state NMR, and extended X-ray absorption fine structure (EXAFS) spectroscopies, as well as chemical methods. When tetraalkyl group 4 precursors are dosed to silica, typical products after hydrogen treatment include mono- ($(\equiv\text{SiO})_3\text{MH}$) and dihydrides ($(\equiv\text{SiO})_2\text{MH}_2$).

Guided by these observations, atomistic representations of silica-anchored group 4 ions have been attempted by cluster and periodic approaches that use silica models of different types and sizes. Cluster models capture local site structure and approximate the constraints imposed by the larger silica framework. Mono- and dihydride of Zr or Ti have been grafted on clusters composed of two to three silicon atoms for evaluating energy profiles of methane activation, ethylene chain growth and hydrogenolysis of M-alkyl reactions.

Kalhor et al. investigated the reactivity of similarly modeled Zr-hydrides towards N$_2$O and CO$_2$ probe molecules and found predicted IR and NMR signatures to be consistent with experimental observations. $^\beta$-cristobalite is a popular choice for describing a silica support, because it can be simply represented within a supercell, it incorporates the constraints of the bulk oxide, and its (111)- and (001)-facets have local order similar to amorphous silica, based on X-ray diffraction observations. Approximate models of amorphous silica have been constructed through molecular dynamics simulations starting from a fully hydroxylated $\beta$-cristobalite surface or other siliceous structures. Reactivity is reported to be sensitive to the details of the support model, whether represented as a cluster, a pseudo-amorphous structure, or an ordered $\beta$-cristobalite surface. The “right” balance of strain, topological orientation, and relative site abundance are all reported to have impact on reactivity. In general, there is no agreement on appropriate strategy or exact relationship between representation of anchoring site and reactivity.

From the available experimental and computational evidence, supported
metal hydrides catalyze olefin chain growth through olefin insertion into M−H bonds (reaction 1) and into M−C bonds (reactions 2):

\[
\begin{align*}
M−H + C_2H_4(g) & \longrightarrow M−C_2H_5 \\
M−C_2H_5 + C_2H_4(g) & \longrightarrow M−C_4H_9
\end{align*}
\]

Termination may occur through hydride elimination to metal (reaction 3a), chain transfer to a monomer (reaction 3c),\(^{55}\) or alkyl elimination (reaction 3b):\(^7-9\)

\[
\begin{align*}
M−C_4H_9 & \longrightarrow M−H + C_4H_8(g) \\
M−C_4H_9 & \longrightarrow M−C_2H_5 + C_2H_4(g) \\
M−C_4H_9 + C_2H_4(g) & \longrightarrow M−C_2H_5 + C_4H_8(g) \\
M−C_4H_9 + C_2H_4(g) & \longrightarrow M−C_2H_3 + C_4H_{10}(g)
\end{align*}
\]

Lastly, ethylene-mediated alkane elimination (reaction 3d) has been proposed as a competing termination step, based on early computational work.\(^{54,56}\)

Besedin et al. compared pathways relevant to ethylene polymerization (reactions 1, 2) on cluster models of Zr mono- and dihydrides.\(^{33}\) They reported activation energies for insertion of ethylene into M−C bonds (reaction 2) to be greater than insertion into the M-hydride (reaction 1), making the former rate limiting for chain growth. Similar models of Ti mono- and dihydrides predict M−C insertion barriers to be greater than for Zr,\(^3\) suggesting a role of the metal ion in controlling chain growth. Their work did not comment upon the role of termination pathways (reactions 3a-3d).

Kaminsky et al.,\(^{57}\) Hoffman et al.,\(^{58}\) and Kissin et al.\(^{59}\) reported that co-fed H\(_2\) reduces the polymer average molecular weight relative to a pure ethylene feed, suggesting that hy-
drogenolysis of the M–R bond competes with chain growth:

\[
M-R + H_2(g) \rightarrow MH + RH
\]  \[ (4) \]

Reaction 4 is a σ-bond metathesis and results in hydrogenolysis of the M-alkyl group. Prior first principles studies have focused on M-butyl hydrogenolysis to form butane in the context of chain termination.\(^3\)\(^,\)\(^{33}\) The relative contributions of reaction 4 and reactions 2, 3a, 3b, 3c and 3d will depend on relative activation energies and reaction conditions, highlighting the need for microkinetic modeling to identify combinations of metal ions and conditions that yield desirable product ranges. Other side reactions, like reinsertion of olefin products that lead to chain walking, isomerization, and methane (see Scheme S1), can influence product topology, type and final properties but are less relevant to intrinsic average molecular weight, which depends upon the competition between chain growth and termination.\(^2\)

To address this need, here we use supercell DFT models to compare ethylene chain growth and termination pathways (reactions 1 to 4) on group 4 metal hydrides grafted on silica. We construct models to probe sensitivity of energetics to metal ion identity and nature of anchoring site. We find non-periodicity in kinetics with Zr sites having the lowest activation energies for all reaction steps, followed by Hf and Ti sites, irrespective of the hydrides considered. However, we observe that chain growth kinetics are sensitive to host silica ring size. We use the DFT results as inputs to microkinetic models to predict turnover frequencies and degree of polymerization (\(P_n\)) as a function of metal ion, site environment and hydrogen pressures at various temperatures. We show that rate and \(P_n\) are sensitive to both metal ion and anchoring site. We conclude that these isolated ions are candidates to synthesize fuel range to polymeric products from ethylene, given the control is exercised over synthesis protocols, reaction conditions and feed composition.
2 Methods

2.1 Computational Details

Plane-wave, supercell DFT calculations are performed using the Vienna Ab Initio Simulation Package (VASP),\textsuperscript{60–63} and projector augmented wave\textsuperscript{64} treatment of core-valence interactions. All systems studied are closed shell and were treated non-spin-polarized using the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation (GGA).\textsuperscript{65,66} The Brillouin zone is sampled at the $\Gamma$ point, plane waves included to a cutoff of 400 eV, and self-consistent field electronic energies converged to $10^{-6}$ eV. Atomic forces are converged to less than 0.05 eV/Å using a conjugate gradient algorithm. Transition states are constructed using a climbing image nudged elastic band (CI-NEB)\textsuperscript{67,68} by linearly interpolating between initial and final structures. Final clean up of transition states was performed using a quasi-Newton (variable metric) optimization or the dimer method.\textsuperscript{69} Transition states are confirmed through harmonic frequencies and of visual inspection of imaginary modes in graphical interface of Atomic Simulation Environment (ASE).\textsuperscript{70} Harmonic vibrational frequencies of the species are computed by finite difference with a step size 0.01 Å, including all adsorbate atoms, metal atom, and/or oxygens of first coordination sphere. Free gas molecules are put in $15 \times 15 \times 15 \text{Å}^3$ cubic cells; energies are given in Table S1. Electronic energies of reaction intermediates and transition states are reported in Tables S7, S13, S19 and reaction and activation energies for elementary steps in Tables S8, S14, S20. All energies reported in electron volts (eV) where 1 eV = 23.06 kcal mol$^{-1} = 96.5$ kJ mol$^{-1}$. Molecular visualizations are created using VESTA.\textsuperscript{71}

We built baseline silica surface models starting from cubic (Fd3m) $\beta$-cristobalite (Fig. S1a).\textsuperscript{72} Within the optimization parameters used here, the relaxed bulk lattice constant is 7.23 Å (experimental: 7.16 Å). The 1% overestimation is typical for gradient-corrected functionals.\textsuperscript{27,73} Silica surfaces having Si-OH groups are created by cleaving Si–O bonds of $\beta$-cristobalite
along (111) and (001) planes and saturating oxygen and silicon dangling bonds with H and OH, respectively. Fully relaxed slabs are shown in Figures S1b and S1c. The surface hydroxyl density of the (111) and (100) models are 3.8 and 7.6 OH/nm², respectively. Metal complexes are anchored on these surface hydroxyl or silanols (Si–OH). We also reconstruct these surfaces to modify the support environment around the metal sites. Overall, we compare three distinct metal hydride site models (Fig. S2). The first two models are of (≡SiO)₃MH situated on three Si–OH groups of isolated silanols (separated by –O–Si–O– bonds) and of vicinal silanols (separated by –O– bonds) on (111) silica surface, while the third is of (≡SiO)₂MH₂ anchored on a pair of vicinal Si–OHs of (001) silica. We refer to sites as a-bmr (≡SiO)₄₋ₙMHₙ where a is the number of rings and b is the membered ring (mr) size formed by consecutive M–OSi bonds with the silica support. Further model details are provided below.

2.2 Microkinetic models

We use the DFT results to parameterize mean-field microkinetic models. The net rate of surface reaction j over time t is written as:

\[
    r_j = k^+_j \prod_{+j} \theta_i^{-c^+_{ij}} \prod_{+j} P_i^{-c^+_{ij}} - k^-_j \prod_{-j} \theta_i^{c^-_{ij}} \prod_{-j} P_i^{c^-_{ij}}
\]  

(5)

where \(c_{ij}\) is the stoichiometric coefficient for species \(i\) in reaction \(j\). The forward and backward reactions are represented as \(+j\) and \(-j\), respectively. \(k_j\) is the rate constant and \(\theta_j\) and \(P_j\) are the coverages and pressures of different species involved in reaction \(j\), respectively.

The coverage is conserved for a surface:

\[
    \theta_* + \sum_i \theta_i = 1
\]

(6)

where \(\theta_*\) is the coverage of free sites. At steady state, \(\sum_j c_{ij} r_j = 0\), giving linear algebraic equations that are solved symbolically with the SymPy library and then numerically.
in Python\textsuperscript{76} to obtain steady-state coverages at each temperature and pressure condition. Steady state rates (s\textsuperscript{−1}) or turnover frequencies (TOF) are obtained from these coverages.

Rate constants for non-activated adsorption of species \(i\) are calculated using the Hertz-Knudsen equation (eq. 7), where \(\alpha'\) is a sticking coefficient that we take as unity, \(m_i\) is the molecular weight of the adsorbing species, and \(k_B\) is the Boltzmann constant, \(T\) is the temperature, and \(A\) is the area per free site, which we approximate as the surface area of the unit cell. This approximation likely exaggerates \(A\), thus increasing absolute absorption rates, but is unlikely to influence reactivity trends.

\[
k_{\text{ads},i} = \frac{\alpha'A}{\sqrt{2\pi m_i k_B T}} \tag{7}
\]

Desorption rate constants are written assuming reaction equilibrium:

\[
k_{\text{des},j} = \frac{k_{\text{ads},i} P^0}{K_j(T)} \tag{8}
\]

where \(K_j(T)\) is the equilibrium constant of reaction \(j\), given by

\[
K_j(T) = \exp\left(-\frac{\Delta E_{\text{DFT}} + \Delta E_{\text{ZPE}} - T \Delta S^\circ_{\text{ads},i}(T)}{k_B T}\right) \tag{9}
\]

\(\Delta E_{\text{ZPE}}\) is the zero-point energy (ZPE) correction added to the electronic energy change \(\Delta E_{\text{DFT}}\). Similar to Toch \textit{et al.},\textsuperscript{77} we take the entropy of physisorption, \(\Delta S^\circ_{\text{phys},i}(T)\) to be 

\(\frac{-1}{3}S^\circ_{\text{trans},i}(T)\), where \(S^\circ_{\text{trans},i}(T)\) is the translational entropy of the gas calculated by the Sackur-Tetrode equation.\textsuperscript{78,79}

Surface reaction rate constants \((k)\) are calculated using transition state theory, DFT-computed and ZPE corrected activation energies \(E_{a,j}\) and the entropy change \(\Delta S^\dagger_j(T)\).

\[
k = \frac{k_B T}{h} \exp\left(\frac{\Delta S^\dagger_j}{k_B}\right) \exp\left(-\frac{E_{a,j}}{k_B T}\right) \tag{10}
\]
between a physisorbed species and a transition state is \(-\frac{2}{3}S^\circ_{\text{trans},i}(T)\) and that between a chemisorbed species and a transition state is zero. Test calculations show that the relative entropy changes are similar to those obtained from the harmonic oscillator and rigid rotor approximation for adsorbates. The free energy change of an elementary reaction \(\Delta G^\circ_j\) is approximated as

\[
\Delta G^\circ_j(T) = \Delta E_j^{\text{DFT}} + \Delta E_j^{\text{ZPE}} - T\Delta S^\circ_j(T)
\]  

(11)

Reaction free energies are plotted in Figures S8, S9, S13, S18 and S19.

3 Results and Discussion

3.1 3-4mr \((\equiv\text{SiO})_3\text{MH}\) site construction

We compute the energies to graft model tetraalkyl M(CH\(_3\))\(_4\) precursors to the silica (111) surface of Fig. S1b, whose adjacent Si–OH groups are separated by \(-\text{O}–\text{Si}–\text{O}–\) linkages. The choice of precursor mimics the organometallic precursors typical for grafting metals. Grafting creates covalent M–O–Si linkages, resulting in \((\equiv\text{SiO})_n\text{M(CH}_3\text{)}_{4-n}\) species that vary in their degree of coordination to the support, \(n\) (details on page 5 in Supplementary Information). Fig. S3 shows the relaxed structures for \(n = 1, 2, 3\) and Tables S2 has their energies. Energies of successive grafting steps of Zr(CH\(_3\))\(_4\) precursor on (111) surface (Fig. S4a) indicate that Zr species tri-coordinated to the support \((n = 3)\) is the most thermodynamically favored. A parity plot of integral grafting energies for all metal ions (values in Tables S3) against Zr in Fig. S4b highlights exothermic trend to be Ti < Zr < Hf, in line with reported M–O and M–C bond energies (Table S4).\(^80\) Successive grafting energies decrease in magnitude with increasing degree of grafting, likely reflecting accumulated strain.

We next compute the energy to remove residual –CH\(_3\) ligands with hydrogen. Hydrogenolysis of each \((\equiv\text{SiO})_n\text{M(CH}_3\text{)}_{4-n}\) to form the corresponding hydride (Table S2) is exothermic (Table S3). Relaxed \((\equiv\text{SiO})_n\text{M(H)}_{4-n}\), M=Ti, Zr, Hf structures are shown.
in Fig. S5. M–O and M–H bond lengths in the tetrahedral M-hydride sites vary non-periodically as Ti < Hf ≤ Zr, following their ionic radii.\cite{81,82} The average O–M–H angle in (≡SiO)$_3$M(H) also follows the same trend. Overall, Ti sites have the least negative formation energies, referenced to silica (111) and precursor.

Fig. 1 shows a representative modeled metal monohydride, (≡SiO)$_3$MH on silica (111), obtained upon full relaxation. The metal ion forms three M-O-Si bonds to the support and thus, rests upon three 4-membered rings (3-4mr), each containing three Si and metal ion (Si/Si/Si/M). Oxygens atoms are excluded while naming the ring. Adjacent M-O-Si bonds are separated by O-Si-O linkages. We name this model as 3-4mr (≡SiO)$_3$MH, where 3 is for the number of rings it forms with silica and 4 refers to the size of each ring. Computed
M–H stretch vibrations of the 3-4mr (≡SiO)$_3$MH in the harmonic limit agree well with experimentally reported frequencies (Table S5). These results are consistent with the well known ability of hydroxyl covered silica surface to accommodate metal alkyl precursors and their further conversion to thermodynamically stable hydrides.

3.2 Oligomerization intermediates on 3-4mr (≡SiO)$_3$MH sites

To evaluate the sensitivity of ethylene oligomerization to the metal ion, we computed reaction pathways for ethylene insertion and chain growth, steps 1 through 4 in Fig. 2, including the three competing chain termination routes, on the 3-4mr (≡SiO)$_3$MH models. Transition
Figure 3: (a) Cossee-Arlman potential energy surfaces computed and referenced to 3-4mr \((\equiv \text{SiO})_3\text{MH}\) sites and 2 \(\text{C}_2\text{H}_4\) gas molecules for \(M = \text{Ti}\) (black), \(\text{Zr}\) (yellow) and \(\text{Hf}\) (blue). Species numbers correspond to Fig. 2. (b) Structures of 3-4mr \((\equiv \text{SiO})_3\text{MH}\), TS(1) and TS(2). Bond distances in Å and bond angles in °.

states (TS) are labeled according to the corresponding reaction number. Multiple configurations of each intermediate were explored, and the lowest-energy structures and corresponding transition states are shown in Fig. S6. CONTCARs are available in a Zenodo data repository. Based on geometry data in Table S6, Ti species have the widest \(\text{O}^\text{−} \text{M}^\text{−} \text{O}\) angle and the shortest \(\text{M}^\text{−} \text{H}\) or \(\text{M}^\text{−} \text{C}\) bonds. Hf species have slightly shorter bond lengths than Zr species. CI-NEB trajectories are illuminated in Fig. S7. Electronic energies of structures are in Table S7 and DFT-computed reaction and activation energies for elementary steps in Table S8.

Potential energy surfaces (PESs) for ethylene insertion and chain growth are mapped in Fig. 3a. Calculations report ethylene to physisorb to the hydride site (structure 1 in Fig. 2, Fig. 3a) with some distortion of the \(\text{O}_3\text{MH}\) tetrahedron. Binding energies are modestly negative. Ethylene inserts into the \(\text{M}^\text{−} \text{H}\) bond through a four-membered-ring transition state, TS(1) (Fig. 3b), to generate M-ethyl (structure 2). TS(1) structures are relatively insensitive to metal ion, except the noticeable difference in \(\text{Si}^\text{−} \text{O}^\text{−} \text{M}\) angle that is widest for...
Ti. Activation energies relative to the hydride and ethylene range from \(-0.02\) to \(0.12\) eV. Reaction energies from the hydride to the ethyl are slightly greater on Ti (by \(-0.14\) eV) than Zr and Hf (1 in Table S8). Results suggest that ethylene insertion into the hydride will be rapid and roughly insensitive to metal.

Ethylene adsorption at M-ethyl occurs with little distortion of the O₃MC tetrahedron (structure 3 in Fig. 2) and ethylene sits away from and weakly bound to the metal center (Fig. S6 and Fig. 3a, 2* in Table S8). A representative CI-NEB trajectory for migratory insertion of ethylene into M–C bond of M-ethyl via TS(2) on the Hf site forming C-C bond is shown in Fig. S7b. The initially bent butyl chain then rotates to an elongated, zig-zagged M-butyl that is lower in energy (structure 4 in Fig. 2). Migratory insertion into M–C bond has a substantially greater barrier that decreases from Ti > Hf > Zr, in inverse variation to M–C and M–O bond lengths. Ustynyuk et al.³ similarly report higher M–C insertion activation energies for Ti-mono-hydride than Zr on cluster models. Ethylene is closest to Ti in TS(2) (shown in Fig. 3b) due to its smallest ionic radius. The Si–O–Ti angle increases to 171°, 6° more than Si–O–Hf and Si–O–Zr angles. The average strain induced by stretching of Si–O–M angles as the site passes through a TS is measured by \(\langle a \rangle\) and is reported in Table S9. For TS(2), \(\langle a \rangle\) varies with the barrier of migratory insertion into M–C bond and decreases from Ti to Hf to Zr. Thus, a larger \(\langle a \rangle\) indicates a greater structural distortion associated with a larger energy penalty for reaching the TS.

We compare the three termination pathways (reactions 3a-3c) in Fig. 4a, b and c, respectively. Overall, the three termination routes have barriers comparable to or greater than chain growth (dashed line in Fig. 4a-c). Termination by reaction 3a occurs via TS(3a) (structure in Fig. S6) and involves \(\beta\)-H transfer from M-butyl to metal ion. Simultaneous loss of the M–C bond yields 1-butene adsorbed on (≡SiO)₃MH (structure 5 in Fig. 2). Ti has the highest activation energy for this step, followed by Hf and then Zr. Butene binds weakly to the metal ion (3a* in Table S8). This pathway is the reverse of ethylene insertion into M–H bond and there is orientational resemblance between TS(3a) and TS(1).
Transfer of a $\beta$-alkyl fragment to M releases an ethylene molecule from the growing chain (reaction 3b) and thus is the reverse of reaction 2. We replot the computed energy profile of the latter, referenced to M-butyl, 4 in Fig. 4a-c. Activation energies increase from Zr to Hf to Ti and are greater than $\beta$-H to M activation energies by at least 0.55 eV.

TS(3c) for ethylene-assisted termination (reaction 3c) is obtained by coordinating an ethylene to M-butyl and simulating a direct transfer of H from the $\beta$-C of butyl chain to ethylene (CI-NEB in Fig. S7d), yielding 1-butene and M-ethyl. TS(3c) is a 6-membered ring and is geometrically similar on Ti, Zr, Hf (structures in Fig. S6). Fig. 4a-c shows that reaction 3c is slightly exothermic, unlike reaction 3a and 3b. This route is kinetically favored over $\beta$-H transfer to M on Ti-, Zr- and Hf-butyl. However, the entropic cost to coordinate an ethylene to M-butyl also enters into the contribution of this route, as discussed further below.

Hydrogenolysis of the M–C bond via reaction 4 would also terminate the growing chain. We computed $\text{H}_2$ dissociation across M–C bond of M-ethyl (2) to form ethane and restore ($\equiv\text{SiO})_3\text{MH}$ (reaction 4) via TS(4) (Fig. S7e). Fig. 5 shows that C–C bond formation
yielding M-butyl (4) is more exothermic than hydrogenolysis to ethane (reactions 2*, 2, 4*, 4 in Table S8). Barriers are comparable on Zr-ethyl and lower for hydrogenolysis on Ti- and Hf-ethyl. The resultant ethylene hydrogenation ($\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$) is highly exothermic ($-1.40$ eV). Hydrogen will likely impact both overall chain growth and selectivity to olefinic products.

These findings show that the key steps of chain growth and termination by chain transfer to ethylene monomer are highly sensitive to the nature of group-4 metal ion and will impact overall reaction chemistry. Differences in initiation steps and hydrogenolysis also exist, but are modest.

3.3 Oligomerization microkinetics on 3-4mr (≡SiO)$_3$MH sites

We use DFT-computed reaction and activation energies to formulate a fully reversible microkinetic model. Adsorbates are assumed to lose all translational entropy and to retain all
Figure 6: (a) Oligomerization rates ($r$) at $P_{C_2H_4} = 17$ bar against reciprocal temperature ($1/T$) and (b) $\bar{P}_n$ vs temperature ($T$) on 3-4mr ($\equiv$SiO)$_3$MH sites ($M = \text{Ti, Zr, Hf}$).

rotational and vibrational entropy; a harmonic oscillator and rigid rotor model yields nearly equivalent results (Fig. S8). We include initiation, chain growth and $\beta$-H transfer to metal with the model. Other termination pathways are kinetically uncompetitive at the temperatures probed here (Fig. S9). Calculations on homogeneous Ti-alkoxide complexes similarly report a preference for $\beta$-H to M termination pathway. As our goal is to compare ideal rates and selectivities to olefin vs paraffin products vs metal, we neglect reinsertion reactions and chain-walking processes, which can lead to isomerized chains and secondary products. Thus, we focus on primary reaction channels, and assume that transport of products from active sites is more rapid than reinsertions.

Steady state rates are computed at zero conversion in pure ethylene feed at 17 bar pressure to capture the intrinsic activities. Computed turnover frequencies (TOFs) are shown as an Arrhenius plot in Fig. 6. TOFs vary as Zr > Hf > Ti, opposite the apparent activation energy trends. Fig. S10 shows that Hf-ethyl and Ti-ethyl are the most abundant surface intermediate (MASI) at all temperatures, while MASI evolves from Zr-butyl to Zr-ethyl with increasing $T$. 

To identify the elementary steps most responsible for controlling the dimerization rates, degree of rate control (DRC) analysis is performed. Rate sensitivity to specific reactions is calculated as $X_{RC,j}$ (eq. 12) by changing the forward ($k_{+j}$) and reverse ($k_{-j}$) rate constants of step $j$ simultaneously by 2%, and monitoring the change of the overall rate $r$ with respect to the reference rate, $r_0$. Rate constants of other steps and the equilibrium constant, $K_j$, are kept constant.

$$X_{RC,j} = \frac{\partial \ln r}{\partial \ln k_{j}} \approx \frac{r - r_0}{0.02 \times r_0}$$

(12)

M–C insertion is rate controlling on the TiH and HfH site (Fig. S11) at all temperatures, while $\beta$-H termination limits the ZrH rate at low $T$ and M–C insertion at higher $T$.

We employ DFT rate constants to first estimate the degree of polymerization ($\bar{P}_n$) promoted by each metal site on reaction with olefins and in absence of H$_2$. The $\bar{P}_n$ model assumes chain growth occurs with a probability of propagation, $\alpha$, calculated by steady state mole balance applied to a M-alkyl site assuming all reactions are irreversible and rate constants for chain growth, $k_{cc}$ and termination, $k_{term}$ are independent of chain length (eq. S.11, details in SI, page 21). $\bar{P}_n$ value for ethylene only feed expresses the average number of oligomeric units in the olefinic product:

$$\bar{P}_n = \frac{1}{1 - \alpha} = 1 + \frac{k_{CC}}{k_{term}}PC_2H_4$$

(13a)

$$\bar{P}_n = 1 + \exp \left( \frac{\Delta S_{CC}^{f} - S_{term}^{f}}{k_B} \right) \cdot \exp \left( \frac{E_{a,term} - E_{a,CC}}{k_BT} \right) PC_2H_4$$

(13b)

Eq 13b deconvolutes the entropic and activation energy contributions to $\bar{P}_n$. Calculated $\bar{P}_n$ are shown in Fig. 6b and follow Ti $\leq$ Hf $<\text{Zr}$. $\bar{P}_n$ is a decreasing function of temperature and is greatest on Zr. Thus, within the 3-4mr site model, ZrH is expected to be a more effective catalyst than TiH or HfH, each of which would have little to any oligomerization activity. Such small $\bar{P}_n$ stands in contrast to experimental observations of polymerization by group-4 metal hydrides on silica.$^{1,5,6,11}$ $\bar{P}_n$ on a 3-4mr ZrH site at low ethylene pressure
Figure 7: Total $P_n$ on 3-4mr ($≡$SiO)$_3$ZrH site and relative contributions of olefin (green) and paraffin (red) fractions to it against $P_{H_2}/P_{C_2H_4}$ at $T = 298$ K and total pressure of 17 bar.

is approximately one (Fig. S12b). This observation suggests that some feature of the model other than the metal itself is relevant to the catalysis.

Hydrogenolysis will compete with $\beta$-H elimination with co-fed $H_2(g)$. To incorporate this competition into the $P_n$, $\alpha$ is recast as $\alpha_{H_2}$ (eq. 14a and eq. S.12). The contributions of olefin and paraffin to total $P_n$ (computed with $\alpha_{H_2}$) are obtained by multiplying this $P_n$ by the ratio of individual fraction’s production rate to the total rate of product formation:

$$\alpha_{H_2} = \frac{k_{cc}P_{C_2H_4}}{k_{cc}P_{C_2H_4} + k_{term} + k_{hyd}P_{H_2}} \quad (14a)$$

$$\text{Olefinic Product} = P_n \cdot \frac{k_{term}}{k_{term} + k_{hyd}P_{H_2}} \quad (14b)$$

$$\text{Paraffin Product} = P_n \cdot \frac{k_{hyd}P_{H_2}}{k_{term} + k_{hyd}P_{H_2}} \quad (14c)$$

We vary $P_{H_2}/P_{C_2H_4}$ such that the total pressure is always 17 bar and trace the resultant modulation in $P_n$s at 298 K and 473 K. Rate constants are computed from entropy-corrected energy profiles (Fig. S13). At 298 K, a decrease in $P_n$ can be seen for 3-4mr ($≡$SiO)$_3$ZrH site along with increasing dominance of paraffinic products even when small amount of hydrogen
Figure 8: (a) Top and side views of 3-3mr (≡SiO)_3Zr site. (b) Comparison of 3-4mr (yellow) and 3-3mr (purple) ZrH ethylene dimerization PESs computed and referenced to the site and number of C_2H_4 molecules reacting with it. Species numbers correspond to Fig. 2. (c) Migratory insertion into M–C bond (purple) and hydrogenolysis (pink) pathways on 3-3mr (≡SiO)_3ZrH sites.

is added (0-0.1 molar ratio, Fig. 7). The same behavior is seen for Ti and Hf (Fig. S13), but the decline in $\bar{P}_n$ is not significant. $\bar{P}_n$ at 473 K on the three 3-4mr (≡SiO)_3MH sites in Fig. S13 is close to unity and the sites are inactive for ethylene hydrogenation.

### 3.4 Influence of anchoring site

To explore the sensitivity of the results above to silica anchoring site, we considered a model in which the M ion is anchored via three 3-membered-rings (3-3mr) to silica (Fig. 8a). We adopt the reconstructed silica (111) facet to represent the host site (Fig. S14), yielding an environment similar to prior cluster models, and focus on M=Zr for the comparisons. Fig. S16 reports structures and Tables S10 and S11 report energies to form (≡SiO)_n-Zr(CH_3)_4-n (n = 1 – 3) by Zr(CH_3)_4 grafting and hydrogenation to (≡SiO)_n-Zr(H)_4-n (plot in Fig. S15a). Grafting energies are less exothermic than on the more open 3-4mr site (parity plot in Fig. S15b), as is hydrogenolysis. Bond distances are similar across the two models, but Zr–O–Si angles are less obtuse at the more constrained 3-3mr site. The M–H stretch frequency is red shifted 36 cm$^{-1}$ relative to the corresponding 3-4mr (≡SiO)_3ZrH.
Figure 9: (a) Oligomerization rate ($r$) vs reciprocal temperature ($1/T$) and (b) Log $P_n$ vs temperature ($T$) on 3-4mr, 3-3mr ($≡\text{SiO})_3\text{ZrH}$ and 1-3mr ($≡\text{SiO})_2\text{Zr(Et)H}$ sites at $P_{\text{C}_2\text{H}_4} = 17$ bar.

We computed the same ethylene insertion and termination pathways on the 3-3mr ($≡\text{SiO})_3\text{ZrH}$ site. Structures are in Fig. S17, bond distances and angles in Table S12, energies in Table S13, and reaction and activation energies in Table S14. Fig. 8b compares reaction profiles on the 3-3mr and 3-4mr sites. Energies of intermediates are nearly the same in the two models, while olefin physisorption (points 1, 3, and 5) is somewhat more exothermic within the more strained 3-3mr model. Activation barriers for chain growth (TS(2)) and for the three termination routes TS(3a-c) are 0.2 eV less within the 3-3mr model as is the extent of $⟨a⟩$ as the TSs are approached (Table S15). The O–M–H angle increases 8° from the 3-4mr to the 3-3mr model, reflecting an increase in access of olefin to the metal site in the latter case. $β$-H transfer has the lowest activation barrier of all termination routes independent of the site model. In contrast, ethylene insertion has a lower activation energy than hydrogenolysis in the 3-3mr model (Fig. 8c), opposite that observed for the 3-4mr case.

To compute oligomerization rates, we again took $β$-H transfer to M to be the dominant termination pathway based on a free energy analysis (Fig. S18a,b) and computed rates using the same initiation, growth, and termination model. Fig. 9a compares computed rates on
the 3-3mr and 3-4mr sites at elevated ethylene pressure. Rates are two- to three-orders of magnitude greater on the 3-3mr site. DRC analysis reports the same shift from β-H termination to ethylene insertion with increasing temperature (Fig. S18d), in correspondence with a shift of MASI (Fig. S18c) from Zr-butyl to Zr-ethyl. The ethylene-only $\bar{P}_n$ on the 3-3mr site (Fig. 9b) is similarly significantly increased than over 3-4mr site (Fig. 6c) at 17 bar. Performance is thus expected to be highly sensitive to anchoring site. The high activity associated with the more constrained anchoring site is consistent with the observation that high temperature dehydroxylation of silica creates smaller and more active anchoring sites.21,22,38,89,90

Silica-anchored zirconium hydrides are reported to polymerize ethylene at near-ambient temperatures.6,11 Calculated $\bar{P}_n$ at the 3-3mr ZrH site at 0.02 and 0.27 bar (Table S16 and Fig. S12b) are consistent with these experimental observations. At higher ethylene pressures, bimolecular reactions (reactions 3c, 3d) as well as co-adsorbed ethylene intermediates91 could compete with the M–C insertion and unimolecular β-H transfer reactions, introducing errors into $\bar{P}_n$.92,93 We re-computed TS(3a) with co-adsorbed ethylene (bim-TS(3a), Fig. S17) and found the activation energy to be comparable to that of chain transfer to monomer (TS(3c)). The activation energy for ethylene-mediated paraffin elimination (reaction 3d, Fig. S17) is also similar to chain transfer to monomer (Tables S13 and S14). Relative activation energies are consistent with prior calculations.31,33 The activation free energies of all five termination routes at 298 and 473 K are reported in Table S16 along with corresponding consequences for $\bar{P}_n$. $\bar{P}_n$ is insensitive to the incorporation of these additional routes. We conclude that unimolecular β-H transfer is the dominant termination route and the 3-3mr ZrH site can be tuned from a polymerization active site at room temperature to selective oligomerization site at higher temperatures at appropriate pressure.

To evaluate the sensitivity of results to co-fed H$_2$, we report the $\bar{P}_n$ and olefin/paraffin contributions on the 3-3mr site vs $P_{H_2}/P_{C_2H_4}$ at 17 bar total pressure and 298 and 473 K (Fig. 10). The corresponding entropy-corrected potential energy profiles for the three com-
Figure 10: Olefinic (green) and paraffinic (red) product contributions in total $\bar{P}_n$ (blue) on 3-3mr ($\equiv$SiO)$_3$ZrH site vs $P_{H_2}/P_{C_2H_4}$ at 17 bar and (a) 298 K and (b) 473 K.

Competing termination reactions are shown in Fig. S19a and b. At 298 K (Fig. 10a), $\bar{P}_n$ decreases and the contribution of paraffinic products increases even at low hydrogen compositions (0.1 molar ratio), as with the 3-4mr ($\equiv$SiO)$_2$ZrH site (Fig. 7). However, $\bar{P}_n$ on 3-3mr ZrH is approximately two orders of magnitude greater than on 3-4mr ZrH site, even at $P_{H_2}/P_{C_2H_4} = 1$. $\bar{P}_n$ is much less sensitive to $H_2$ at 473 K (Fig. 10b), and the short-chain products are primarily olefinic.

We consider a third site model in which M is anchored to silica through only two oxygen linkages, constructed from a dehydroxylated (001) facet of silica (Fig. S20). Zr(CH$_3$)$_4$ grafting energies to form ($\equiv$SiO)$_2$Zr(CH$_3$)$_2$ are intermediate between the 3-4mr and 3-3mr models (Fig. S21, Tables S17 and S18) and subsequent hydrogenation is exothermic (structures in Fig. S22). Hydrogenation to the dihydride, ($\equiv$SiO)$_2$ZrH$_2$ results in a site anchored via two Zr–O–Si bonds (Fig. 11a) forming a 1-3mr ($\equiv$SiO)$_2$ZrH$_2$ site.

Computed structures and PES for Fig. 11b pathway are provided in Figs. S23 and S24, respectively and energies in Tables S19 and S20. The availability of two Zr–H bonds offers the potential for growth of two chains. Computed barriers to insert ethylene sequentially into these two are both less than 0.1 eV. The more open coordination around Zr enables “agostic” interactions$^{94,95}$ between ethyl hydrogen atoms and Zr, evidenced in reduced distances and
angles; test calculations indicate that these interactions stabilize intermediates by approximately 0.1 eV and cost approximately the same amount at transition states (Fig. S25).

We computed the PES for chain growth starting from \( \equiv \text{SiO})_2\text{ZrEt}_2 \) (Et = ethyl) and termination to 1-butene and \( \equiv \text{SiO})_2\text{Zr(H)Et} \) (Fig. 11b). As shown in Fig. 11c, both steps have activation energies less than those on the 3-4mr and 3-3mr models. Fig. 9a and b show that predicted oligomerization rates and degree of polymerization are greater on the 1-3mr Zr-dihydride than either Zr-monohydride site. This remains true even at lower ethylene pressures and temperature where the site forms polymers (Fig. S12).

Corresponding results for the Ti- and Hf-dihydrides are reported in SI Figs. S23-S28 and Tables S19-S20. Variations with metal follow the same trend as found for the 3-4mr mono-hydride sites.

Figure 11: (a) Top and side view of 1-3mr \( \equiv \text{SiO})_2\text{MH}_2 \) site. (b) Dihydride oligomerization pathways. (c) Parity plot of M–C insertion \( (E_a, C-C) \) and \( \beta \)-H termination \( (E_a, \text{term}) \) barriers on 3-3mr \( \equiv \text{SiO})_3\text{ZrH} \) (purple squares) and 1-3mr Zr-dihydride (orange triangles) sites against those on 3-4mr \( \equiv \text{SiO})_4\text{ZrH} \) (gold circles).
4 Conclusions

Ethylene oligomerization and polymerization performance of heterogenized metal ions are known to be influenced by the metal ion identity, support morphology, and reaction conditions. Here we compare predicted performance across the three group 4 metal ions and three different silica anchoring site models. Microkinetic models based on DFT results show that Zr has the highest intrinsic activity of the three metals (Fig. 6), as measured by oligomerization rate, that activity is modulated significantly by the local support environment (Fig. 9), and further that both the degree of polymerization and fraction of olefinic vs paraffinic products are sensitive to co-fed H$_2$. Table S16, Fig. S12 along with Fig. 9 lay out the selectivity change from polymerization to oligomerization on 3-3mr Zr-monohydride and 1-3mr Zr-dihydride sites going from low to high temperatures under different pressures. Results indicate that anchored Zr ions are promising candidates for high-temperature oligomerization of ethylene, but that product selectivity will require uniformity in anchoring site and control of temperature and hydrogen concentration.

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Conflicts of interest

There are no conflicts to declare.

Supplementary Information

Electronic Supplementary Information (ESI) available: Geometries and structural information, vibrational frequencies, absolute and relative energies, Gibbs free energies, and predicted site coverages in supplementary PDF file. Separate folders for CONTCARs of all structures and python scripts to create potential energy plots, rates, coverages, $\bar{P}_n$ and degree of rate control are shared in Zenodo.83

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The data that support the findings of this study are openly available in Zenodo data repository available at [https://zenodo.org/doi/10.5281/zenodo.11251372](https://zenodo.org/doi/10.5281/zenodo.11251372).