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Multireference Investigations of Ethylene Hydrogenation over Bimetallic Catalysts

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Abstract

Antiferromagnetically coupled bimetallic hydrides are promising catalysts for olefin hydrogenation, but their electronic structure presents a challenging problem for single-reference electronic structure methods. We investigated ethylene hydrogenation by unsupported and silica-supported dinuclear Ni and Fe hydride catalysts using density functional theory (DFT) and GPU-accelerated localized active-space (LAS) multireference methods and multiconfiguration pair-density functional theory (MC-PDFT). For the unsupported dinuclear Ni hydride catalyst, different DFT functionals predict different spin-state orderings along the catalytic cycle, ethylene binding energetics, transition-state barriers, and even different rate-determining step. In contrast, multireference methods provide a consistent description of the spin manifold and reaction

energetics across the pathway, with substantially reduced sensitivity to the choice of on-top functional. The calculations further show that the bridging Ni–H–Ni motif remains intact during ethylene coordination and migratory insertion, in contrast to previously proposed mechanisms involving prior bridge opening. Comparison of supported and unsupported systems reveals strongly metal-dependent support effects. Silica coordination substantially lowers the hydride-transfer barrier in the Ni catalyst, whereas the Fe systems are influenced more strongly by intrinsic metal-centered electronic structure effects. These results show that antiferromagnetically coupled bimetallic hydrides can fall outside the reliable regime of single-reference DFT and require multireference treatments to obtain consistent mechanistic predictions.

1 Introduction

Ethylene hydrogenation is a prototypical reaction and an important platform for understanding fundamental mechanisms of olefin hydrogenation in catalysis.^{1–3} Molecular transition-metal complexes supported on oxide surfaces are particularly attractive because they combine tunable coordination environments with the practical advantages of heterogeneous catalysts.^{4–11} For example, silica-supported organovanadium and iridium catalysts have been shown to hydrogenate alkenes and alkynes efficiently,^{12–14} and supported Ir and Rh hydride complexes promote alkene hydrogenation under mild conditions.^{15,16} Computational studies have also demonstrated that the local support environment can strongly influence the reactivity and electronic structure of supported catalysts.^{17–21}

Dinuclear hydrides are especially interesting because cooperative interactions between two metal centers can alter substrate activation and hydrogen-transfer chemistry. Recently, Czerny et al. reported a silica-supported dinuclear nickel hydride catalyst capable of alkene and alkyne hydrogenation at room temperature.²² The corresponding molecular precursor was previously synthesized by Pfirrmann and co-workers as an antiferro-

magnetically coupled dinuclear Ni hydride complex.²³ The supported dinuclear catalyst was proposed to operate through opening of the bridging Ni–H–Ni motif prior to ethylene insertion and hydrogenolysis. Despite these experimental advances, the molecular-level mechanism of ethylene hydrogenation in dinuclear hydride catalysts remains unresolved.

In particular, it is unclear whether the bridging hydride must open as proposed or can remain intact during catalysis, how strongly the two metal centers cooperate along the reaction coordinate, the identity of the rate-determining step, and how the silica support perturbs the reaction energetics. These questions are electronically challenging because antiferromagnetically coupled transition-metal systems often exhibit substantial near-degeneracy and multireference character. More broadly, previous studies on strongly correlated transition-metal complexes have shown that density functional theory (DFT) can yield qualitatively different spin-state orderings and reaction energetics depending on the chosen exchange-correlation functional.^{24–29} Similar challenges have motivated the use of multireference methods in studies of transition-metal catalysis, including methane activation at metal–oxo centers,²⁶ supported vanadia catalysts,³⁰ and correlated catalytic systems in metal–organic frameworks.^{31–37}

Multireference methods such as complete active space self-consistent field (CASSCF) and restricted active space self-consistent field (RASSCF) explicitly treat static correlation and provide a more appropriate framework for electronically complex catalytic systems.^{38,39} Dynamical correlation can be recovered through second-order perturbation theories such as complete active-space perturbation theory (CASPT2)^{40,41} and *n*-electron valence perturbation theory (NEVPT2).⁴² Their application to realistic catalyst models, however, has historically been limited by computational cost. Localized active-space (LAS) approaches^{43–45} and their recent GPU-accelerated implementations⁴⁶ now make multireference treatments feasible for substantially larger transition-metal systems. In particular, localized-active space state interaction singles (LASSIS)⁴⁷ and multiconfiguration

pair-density functional theory (MC-PDFT)^{48,49} provide a practical route to incorporating inter-fragment and dynamical correlation in multimetallic catalysts.

Here, we investigate ethylene hydrogenation in silica-supported and unsupported dinuclear Ni hydride catalysts together with the corresponding Fe analogues. Using unsupported Ni catalyst as a benchmark for method validation, we first benchmarked LASSCF against CASSCF, and validated MC-PDFT against NEVPT2. We then assessed the sensitivity of the spin-state ordering, ethylene binding, and catalytic barriers to the choice of DFT functionals relative to GPU-accelerated LASSCF/LASSIS/MC-PDFT methods. The calculations show that different density functionals can predict qualitatively inconsistent ethylene binding strengths, and different rate-determining steps and spin-state orderings, whereas the multireference approaches provide a more mechanistically and energetically consistent descriptions throughout the catalytic cycle. The results further indicate that the bridging hydride motif remains intact during ethylene insertion and that support effects are strongly metal dependent.

2 Results and Discussion

2.1 Catalyst model and reaction mechanism

For the silica-supported catalysts, the silica support was truncated to obtain a model that retains the essential electronic effects while remaining computationally tractable. We first modeled the support using a silsesquioxane (SSQ) cage, consistent with cluster models commonly employed for silica-supported catalysts.^{17–21,50–52} The bimetallic hydride unit was grafted onto the SSQ cage through the metal–oxygen bonds, in which the SSQ oxygen atom is bridging the two metal centers, consistent with experimentally proposed silica-supported structure (Figure S1).²² After geometry optimization, the support was further reduced to a smaller silanol-based cluster for the multireference calculations. The truncated model contains one Si atom and four O atoms, with terminal Si–O bonds saturated

by hydrogen atoms (Figure 1a). Natural charge analysis shows nearly identical charge distributions at the active site for the SSQ and silanol models (Table S1). In both models, the two Ni centers carry essentially the same charge, while differences on neighboring H, O, and Si atoms remain below 0.05 e. The silanol cluster therefore reproduces the local electronic environment of the larger SSQ model while substantially reducing the computational cost. The unsupported molecular catalysts contain two bridging hydrides and preserve the same bimetallic core geometry (Figure 1b). All geometry optimizations are performed at the B3LYP/def2-TZVP level of theory;^{53–55} additional details are provided in the Methods section 4.1.

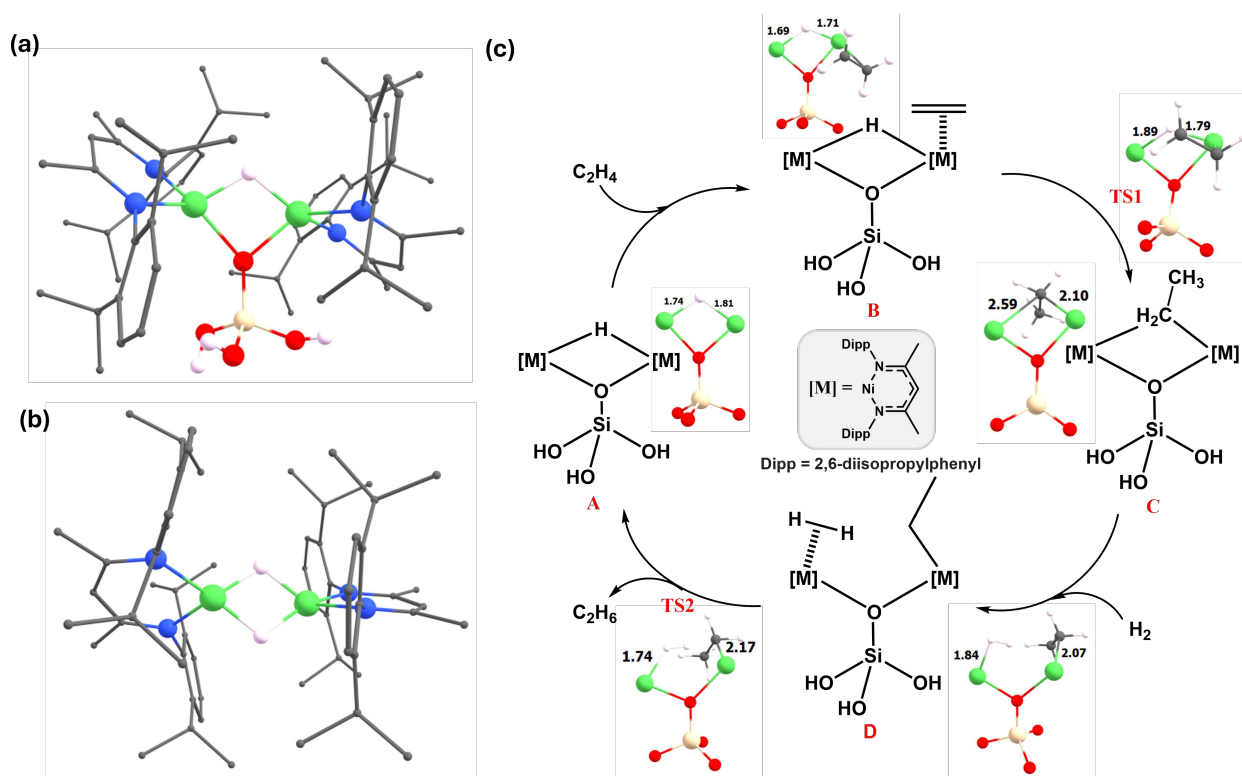


Figure 1: Structures of active catalysts for (a) silica-supported (b) unsupported Ni models. Hydrogens are omitted for clarity. (c) Mechanism of ethylene hydrogenation by silica-supported bimetallic hydride catalysts, with the Ni-H-Ni-silanol motifs displayed alongside the catalytic cycle for clarity while the full structures are shown in SI. Color code: Ni: green, N: blue, O: red, Si: light brown, C: gray, and H: white.

The computed catalytic cycle for the silica-supported Ni system is shown in Figure 1c. Although the structures shown correspond to the silica-supported Ni system, the unsup-

ported and supported Ni catalysts, as well as the two Fe analogues, follow a similar reaction pathway. The active catalyst, **A**, contains a hydride asymmetrically shared between the two Ni centers as the Ni-H-Ni motif. The reaction begins with the binding of ethylene molecule to **A**, forming the ethylene-bound intermediate, **B**. Importantly, the computed mechanism suggests a revision to the previously proposed picture: The experimental paper²² proposed that the Ni-H-Ni bridge first opens up to form a monometallic hydride and an under-coordinated metal site for ethylene binding; nevertheless, this study suggested that the Ni-H-Ni bridge remains intact and participates directly in a cooperative dinuclear pathway.

From intermediate **B**, migratory insertion proceeds through transition state, **TS1**, during which the hydride becomes increasingly associated with the ethylene-coordinated Ni center as C-H bond formation develops. Passage through **TS1** yields ethyl intermediate, **C**, in which the newly formed ethyl fragment remains associated with both Ni centers, although this interaction becomes strongly asymmetric after hydride transfer. Thus, the insertion step proceeds within an overall dinuclear environment rather than through prior dissociation of the Ni-H-Ni bridge.

Subsequent coordination of H₂ to intermediate **C** generates intermediate **D** through cooperative interaction with the dinuclear Ni framework. At this stage, the ethyl fragment preferentially associates with one Ni center, while H₂ activation occurs at the second Ni site. Hydrogenolysis then proceeds through transition state, **TS2**, via concerted H-H bond cleavage and C-H bond formation, leading to release of ethane and regeneration of the original bridging hydride catalyst, **A**.

Overall, the calculations support a cooperative dinuclear mechanism in which the bridging hydride motif remains intact until migratory insertion. Differentiation between the two metal centers emerges only after hydride transfer and during H₂ activation. This mechanistic picture is consistent with prior selective poisoning experiments reported, in which the amount of ethylene converted corresponded to approximately half of the total

Ni sites, supporting the involvement of dinuclear motifs in the hydrogenation mechanism.²² Optimized structures and selected bond distances are shown in Figure S2.

2.2 MC-PDFT benchmarking and validation

We benchmarked the multireference protocol using the unsupported Ni catalyst as a reference system. Specifically, we examined the sensitivity of the reaction-energy profile to active-space size, (n,m) , where n and m correspond to the number of electrons and orbitals in the active space, respectively, assessed the accuracy of the LAS approximation relative to CASSCF, compared MC-PDFT against NEVPT2, and evaluated basis-set effects.

We first examined the dependence of the reaction energetics on the active-space definition. Three active spaces were considered for the Ni system: a minimal LAS(4,4), an intermediate LAS(16,16), and a larger LAS(16,20). Additional details of the active-space construction are provided in Section 4.2. Unless otherwise stated, all benchmark calculations in this section employed a reduced basis partition with def2-TZVP on Ni and def2-SVP on all remaining atoms.

The reaction-energy profiles obtained with the three active spaces differ by less than 1.5 kcal/mol (Figure 2a), indicating weak sensitivity of the energetics to active-space size. Although LAS(4,4) reproduces the overall energetics reasonably well for the unsupported Ni system, it does not yield consistent active orbitals for several intermediates and transition states in the silica-supported Ni catalyst. We therefore employ LAS(16,16) throughout this work. For the Fe systems, the minimal LAS(8,8) active space similarly produced inconsistent active orbitals, whereas LAS(12,12) and LAS(12,20) gave nearly identical energetics, differing by only 0.2 kcal/mol (Figure S3). We therefore adopt LAS(12,12) for both unsupported and supported Fe catalysts.

Next we benchmarked the LAS approximation against CASSCF using the unsupported Ni system and the same basis-set partitioning. Because CASSCF(16,20) calculations were computationally prohibitive, we chose (16,16) active space for both CASSCF

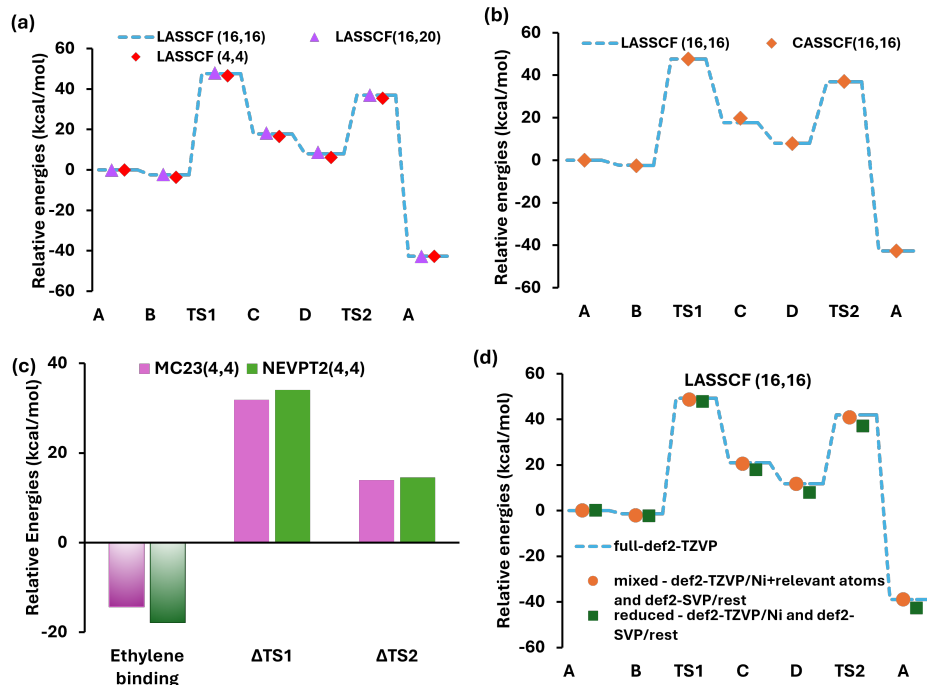


Figure 2: Comparison of reaction energy profile for unsupported Ni catalytic system with (a) LASSCF(16,16), LASSCF(16,20) and LASSCF(4,4), (b) LASSCF(16,16) vs CASSCF(16,16) (c) Computed ethylene binding energies and two transition state barriers ($\Delta TS1$ and $\Delta TS2$), obtained with MC23 and NEVPT2 with (4,4) active space. (e) Comparison of reaction energy profile with different basis set partitions. All the results for plots (a) - (c) use a reduced basis set scheme, i.e., def2-TZVP on Ni and def2-SVP on the rest of the atoms.

and LASSCF for comparison. The LAS(16,16) and CAS(16,16) reaction-energy profiles agree closely (Figure 2b), within 0.5 kcal/mol difference for all species except for intermediate **C**, which differs by 2 kcal/mol. These results show that the localized active-space treatment captures the essential multireference character of the bimetallic catalyst while substantially reducing the computational cost.

We then compared MC-PDFT with NEVPT2 using the tPBE,⁴⁸ tPBE0,⁵⁶ and MC23⁵⁷ on-top functionals. All methods produce qualitatively similar reaction-energy profiles (Figure S4). Among the three on-top functionals, MC23 gives the closest agreement with NEVPT2 for both ethylene binding and transition-state barriers ($\Delta TS1 = E_{TS1} - (E_B + E_{Ethylene})$ and $\Delta TS2 = E_{TS2} - (E_C + E_{H_2})$) (Figure 2c). These benchmark calculations were performed with the minimal active space, LAS(4,4), because of the computational cost of NEVPT2.

Based on this agreement, the scientific inferences are primarily based on MC23 results obtained with LAS(16,16), while tPBE and tPBE0 are used for comparison throughout the manuscript.

Finally, we examined basis-set effects using three basis partitions: (i) a reduced basis treatment with def2-TZVP only on Ni and def2-SVP⁵⁵ on all remaining atoms; (ii) a mixed basis treatment with def2-TZVP on the reactive core (containing Ni atoms, hydrides, the six-membered rings containing Ni, and reacting molecular moieties) and def2-SVP on the surrounding ligand environment; and (iii) full basis set treatment with def2-TZVP on all atoms. Each full def2-TZVP calculation required approximately 6000 min on six GPUs on Aurora,⁵⁸ highlighting the importance of identifying a reduced-cost scheme. The mixed-basis and full def2-TZVP calculations yield nearly identical reaction-energy profiles, differing by less than 0.5 kcal/mol (Figure 2d). In contrast, the reduced-basis scheme systematically underestimates the barriers, with deviations increasing to ~ 5.6 kcal/mol near TS2. These results show that triple- ζ quality basis functions are required primarily on the atoms directly involved in bond breaking and formation, while the extended ligand environment can be described adequately with def2-SVP.

Based on these benchmarks, all subsequent calculations employ the mixed basis partition together with LAS(16,16) for Ni and LAS(12,12) for Fe. Interfragment correlation is incorporated through LASSIS,⁴⁷ and dynamical correlation is included using MCPDFT.⁴⁸

2.3 Spin-state energetics

An accurate description of spin-state energetics is essential for these antiferromagnetically coupled bimetallic systems, where small changes in electronic structure can alter the reaction profile. We therefore examined the spin-state energetics of all intermediates and transition states for the unsupported Ni catalyst using both DFT and multireference methods with the LAS(16,16) active space. The results for the active catalyst, **A**, and the

ethylene-bound intermediate, **B**, are shown in Figure 3, while the remaining spin ladders are provided in Figure S5.

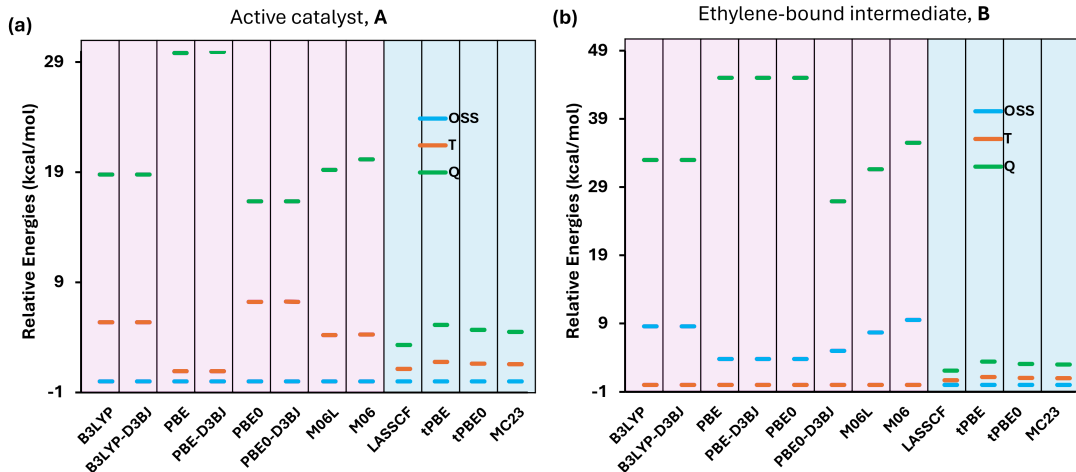


Figure 3: Comparison of the spin-state energetics for (a) active catalyst, **A** and (b) ethylene-bound species, **B**, for the unsupported Ni catalyst, obtained with DFT (pink background) and MR (blue background) methods. For MR results, (16,16) active space is used.

For **A**, both DFT and MR approaches predict an open-shell singlet (OSS) ground state, consistent with the experimentally proposed antiferromagnetically coupled Ni centers in the precursor complex.²³ However, the relative energetics of the low-lying excited spin states vary substantially across the different DFT functionals. Depending on the functional, the triplet state is predicted to lie within ~ 0.5 – 9 kcal/mol of the OSS state, while the quintet spans a broader range of ~ 18 – 30 kcal/mol. In contrast, the MR approaches provide a comparatively more compact and internally consistent description of the spin ladder, with both triplet and quintet states remaining within ~ 6 kcal/mol of the OSS ground state.

Larger differences between DFT and MR descriptions emerge for **B**. While all considered DFT functionals predict a triplet ground state followed by the OSS and quintet states, the MR methods consistently favor an OSS ground state with closely spaced triplet and quintet excitations. Although the energetic differences between the OSS and triplet states are relatively small, the MR approaches provide a more uniform qualitative description

across the catalytic pathway.

This trend extends to the remaining intermediates and transition states (Figure S5). For **TS1** and **D**, both DFT and MR methods predict an OSS ground state. In contrast, for intermediate **C** and **TS2**, the DFT methods favor a triplet ground state, whereas the MR approaches predict an OSS ground state for **C**. For **TS2**, the MR methods identify a quintet ground state, although the OSS and triplet states remain nearly degenerate within ~ 1 kcal/mol. Overall, the DFT spin-state ordering oscillates between OSS and triplet states along the reaction coordinate, whereas the MR approaches provide a more uniform description dominated by OSS character across most intermediates and transition states.

The same qualitative trends are observed for the silica-supported Ni catalyst and for both unsupported and supported Fe analogues. Notably, the predicted OSS ground state for the unsupported Fe catalyst is consistent with experimentally reported antiferromagnetic coupling between the Fe centers in related dinuclear hydride complexes.⁵⁹

2.4 Ethylene binding energy

Ethylene binding in transition-metal catalysts depends sensitively on the treatment of correlation and metal–olefin interactions.^{60–62} To examine the metal–ethylene interaction in intermediate **B**, we computed ethylene binding energies for the unsupported Ni catalyst using several DFT functionals together with the three MC-PDFT on-top functionals and the LAS(16,16) active space (Figure 4a).

Conventional GGA and hybrid-GGA functionals without dispersion corrections predict weak or unfavorable ethylene binding, whereas dispersion-corrected functionals stabilize the ethylene-bound intermediate. Similar behavior is observed for the Minnesota meta-GGA functionals (M06L and M06), which also predict favorable binding. These results indicate that medium- and long-range correlation effects play a major role in ethylene coordination.

The MC-PDFT calculations also predict favorable ethylene binding. Although the cor-

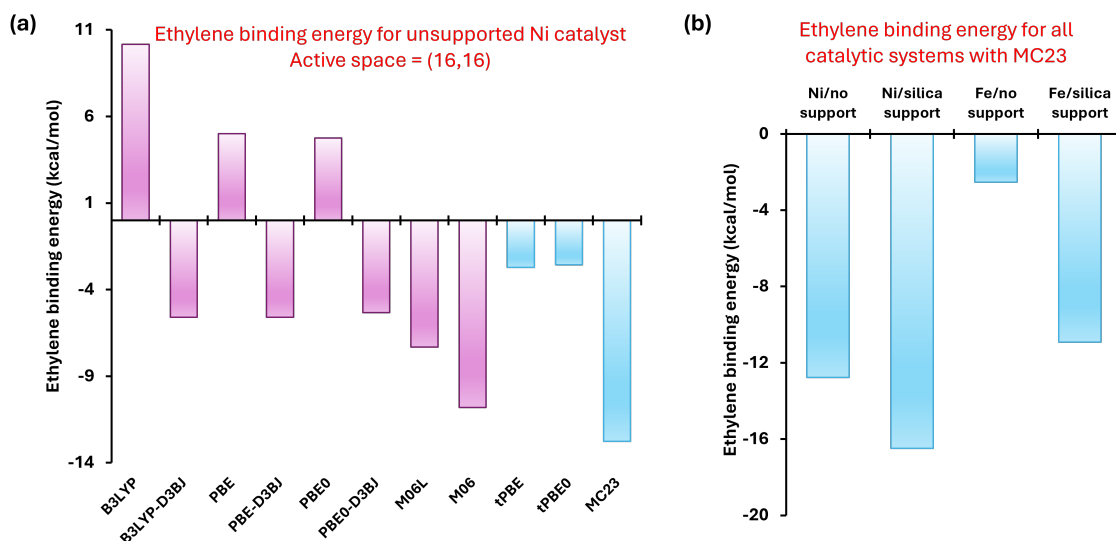


Figure 4: (a) Comparison of ethylene binding energy for unsupported Ni catalyst with different DFT functionals (pink) and MC-PDFT on-top functionals (blue) with (16,16) active space. (b) Ethylene binding energy for all catalytic systems obtained with MC-PDFT/MC23 functional with (16,16) active space for Ni systems and (12,12) for Fe systems.

responding single-reference PBE- and PBE0-based DFT calculations give weak or unfavorable binding, the analogous tPBE and tPBE0 calculations stabilize the ethylene-bound intermediate. The strongest binding is predicted by MC23. Overall, the results show that the description of ethylene coordination is highly sensitive to the electronic structure treatment.

We next compared the MC23 ethylene binding energies across all four catalytic systems (Figure 4b). All systems exhibit favorable ethylene binding. In both the Ni and Fe catalysts, silica coordination strengthens ethylene binding relative to the unsupported analogues, indicating that the support electronically stabilizes the coordinated olefin intermediate. The experimentally observed room-temperature activity of the silica-supported Ni catalyst²² is consistent with favorable ethylene binding.

2.5 Transition-state barriers

Having established that MC23 reproduces NEVPT2 reaction energetics well, and that MC-PDFT provides a more consistent description of spin-state ordering and ethylene binding than DFT, we next examined the transition-state barriers. We compare the two barrier heights (ΔTS1 and ΔTS2), of the unsupported bimetallic Ni system across different DFT and MR methods, as summarized in Figure 5a. The computed ΔTS1 exhibits pronounced functional dependence, spanning approximately 5-19 kcal/mol across the functionals. This wide spread indicates substantial functional sensitivity for the step associated with hydride migration and C-H bond-forming reorganization. In contrast, MC-PDFT gives a substantially narrower range of $\sim 27\text{--}32$ kcal/mol across the three on-top functionals, indicating reduced functional sensitivity of the three PDFT functionals. DFT functionals also predict significantly lower ΔTS1 barriers than MC-PDFT. For ΔTS2 , the spread across methods is smaller, with DFT and MC-PDFT values differing by only $\sim 5\text{--}6$ kcal/mol.

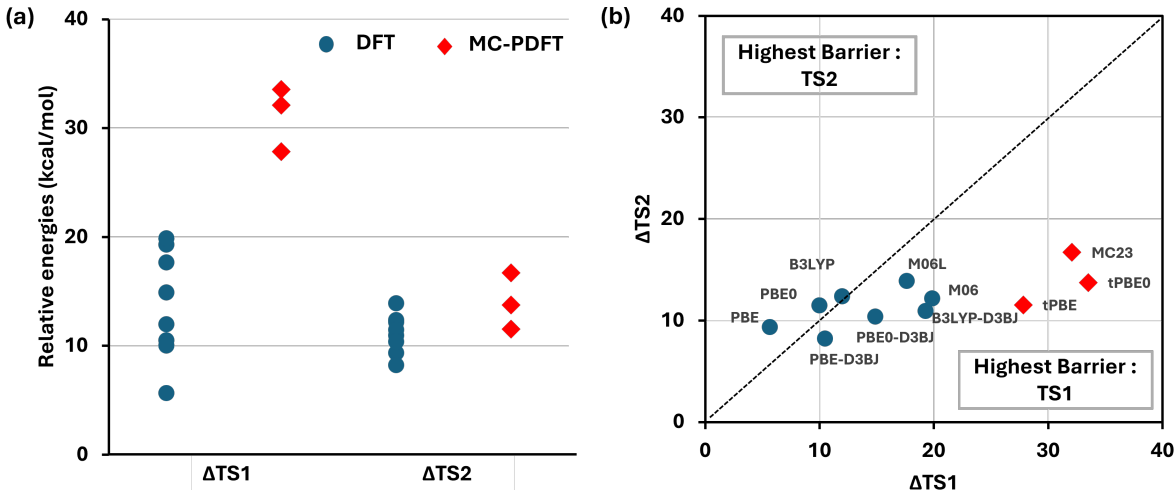


Figure 5: (a) Comparative distribution of calculated barrier heights (ΔTS1 and ΔTS2) from DFT (blue) and MC-PDFT (red) functionals for the two transition states (b) Computed ΔTS1 and ΔTS2 for unsupported Ni system.

The predicted rate-determining step depends strongly on the electronic structure method. B3LYP, PBE, and PBE0 predict **TS2** as rate limiting, whereas dispersion-corrected and

Minnesota functionals predict **TS1** (Figure 5b). In contrast, all MC-PDFT calculations consistently identify **TS1** as the higher barrier along the reaction coordinate. Although dispersion-corrected DFT recovers the same qualitative assignment, the corresponding barriers remain systematically lower than the multireference values.

We next examined how the barriers change with support and metal identity using MC23 (Figure 6 and Table 1). Results obtained with tPBE and tPBE0 show the same qualitative trends (Figure S6). The silica support strongly affects the Ni catalysts. For the

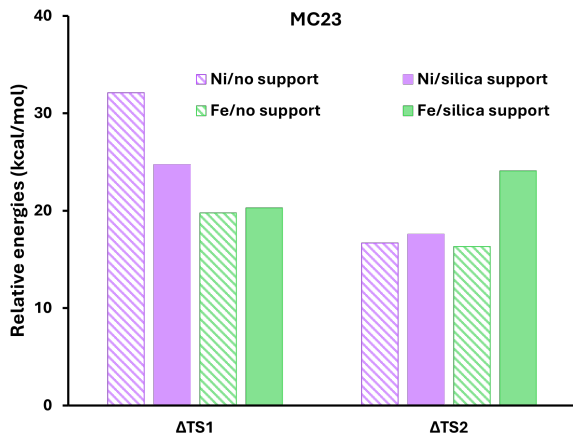


Figure 6: Computed transition state barriers, $\Delta TS1$ and $\Delta TS2$, for all the four studied catalysts from MC-PDFT with MC23 on-top functional. For Ni and Fe systems, the active space of (16,16) and (12,12) is used respectively. The dotted and solid bars represent catalysts without and with silica-support respectively. The purple and green colors correspond to Ni and Fe systems respectively.

unsupported Ni system, $\Delta TS1$ is 32.1 kcal/mol, whereas silica coordination lowers the barrier to 24.7 kcal/mol. In contrast, $\Delta TS2$ changes only slightly, increasing from 16.7 to 17.6 kcal/mol. The support therefore selectively stabilizes the hydride-transfer transition state and lowers the overall kinetic barrier. The Fe systems show qualitatively different behavior. The unsupported Fe catalyst already exhibits substantially lower barriers, with $\Delta TS1$ and $\Delta TS2$ of 19.7 and 16.3 kcal/mol, respectively. Upon silica coordination, $\Delta TS1$ changes only marginally, while $\Delta TS2$ increases to 24.1 kcal/mol, shifting the rate-determining step from **TS1** to **TS2**. Thus, whereas silica lowers the dominant barrier in the Ni systems, it destabilizes the later hydrogenation step in the Fe catalysts.

Table 1: Computed transition state barriers (kcal/mol), ΔTS1 and ΔTS2 , from MC-PDFT with MC23 functional across the four studied catalytic systems with the active space of (16,16) for Ni and (12,12) for Fe systems.

Catalyst	ΔTS1	ΔTS2
Ni/no support	32.1	16.7
Ni/silica support	24.7	17.6
Fe/no support	19.7	16.3
Fe/silica support	20.3	24.1

These results indicate that support effects are strongly metal dependent. In the Ni systems, the support primarily stabilizes the hydride-transfer transition state. In the Fe systems, the reaction energetics depend more strongly on the intrinsic electronic structure of the bimetallic core.

Although direct experimental analogues of the present Fe hydride models remain limited, prior studies on silica-supported bimetallic Fe catalysts have reported enhanced olefin hydrogenation activity relative to related monometallic systems.⁶³ Importantly, those experimentally studied catalysts differ substantially from the present Fe hydride models in coordination environment and bridging ligand identity, as the reported systems are derived from mesitylene-bridged Fe dimers that undergo support-dependent restructuring upon grafting, whereas the present models retain a more structurally defined hydride-bridged Fe_2 framework. Consequently, the comparison should be regarded as qualitative rather than one-to-one. Nevertheless, the experimental observations support the broader conclusion that cooperative Fe–Fe interactions can facilitate hydrogenation chemistry, while the present calculations additionally highlight the sensitivity of the catalytic energetics to support-induced electronic effects.

To further characterize these systems, we examined two complementary analyses: the N diagnostic, which quantifies the degree of multireference character where $N > 0.1$ implies significant MR character,⁵⁷ and Mulliken charge analysis, which probes the redistribution of electron density upon support coordination. Most unsupported Ni and Fe species show substantial MR character ($N = 0.12 - 0.22$), whereas the silica-supported ana-

logues exhibit generally smaller values ($N=0.05\text{--}0.12$) (Table S2 and Figure S8). The only exception is the **TS2** for unsupported Ni, which has an anomalously low $N=0.03$, consistent with its quintet, more single-configurational ground state.

Mulliken charge analysis shows that both Ni and Fe become more positively charged upon coordination to silica, while the coordinating oxygen becomes substantially more negative than the remaining oxygen atoms of the support (Table S3 and Figure S9). These results indicate electron withdrawal from the bimetallic core through metal–oxygen bonding.

Overall, the calculations identify Fe-based bimetallic hydrides as promising alternatives for hydrogenation catalysis and show that antiferromagnetically coupled bimetallic systems can exhibit strong sensitivity to the underlying electronic structure treatment.

3 Conclusions

We investigated ethylene hydrogenation in silica-supported and unsupported dinuclear Ni and Fe hydride catalysts using DFT and multireference methods. Benchmark calculations on the unsupported Ni system showed good agreement between MC-PDFT MC23 on-top functional and NEVPT2, supporting the use of MC23 for efficiently incorporating dynamical correlation effects. The calculations show that the bridging hydride motif remains intact during ethylene coordination and migratory insertion, supporting a cooperative dinuclear mechanism rather than prior M-H-M bridge opening.

The electronic structure of these antiferromagnetically coupled systems is highly sensitive to the computational method. Different density functionals predict different spin-state orderings, ethylene binding energetics, transition-state barriers, and even different rate-determining steps. In contrast, the multireference methods provide a substantially more consistent description of the catalytic cycle, with reduced sensitivity across the MC-PDFT on-top functionals.

The results from MC23 (MC-PDFT) further point to strongly metal-dependent support effects. Silica coordination lowers the hydride-transfer barrier in the Ni catalysts, whereas the Fe systems are governed more strongly by intrinsic metal-centered electronic structure effects. The Fe catalysts also exhibit lower overall barriers than the corresponding Ni systems.

These results show that antiferromagnetically coupled bimetallic hydrides can fall outside the reliable regime of single-reference DFT. In these systems, multireference treatments are required to obtain consistent spin-state ordering, reaction energetics, and mechanistic assignments.

4 Methods

4.1 DFT calculations

Geometry optimizations were carried out using DFT with the B3LYP functional^{53,54} and def2-TZVP⁵⁵ basis set along with AUTOAUX for the automatic generation of auxiliary basis set.⁶⁴ RIJCOSX was used to speed up the calculations.⁶⁵ Stationary points were characterized by vibrational frequency calculations: minima exhibited no imaginary frequencies, while transition states were confirmed by the presence of a single imaginary frequency corresponding to the reaction coordinate. The thermal corrections of the gas phase molecules were calculated at 298.15 K and 8 bar pressure, consistent with experimental conditions.²² We discuss electronic energy barriers (Table S4-S9) throughout the main text to directly compare the differences between DFT and MR methods at the electronic-structure level. Gibbs free energies were also evaluated and are reported in the SI (Table S10-S12). To preserve a uniform thermochemical treatment across methods, the thermal correction for each stationary point was taken from the corresponding B3LYP value and added to the DFT and multireference electronic energies. Because full multireference geometry optimizations remain computationally prohibitive for systems of this size, all mul-

reference energetics were evaluated on DFT-optimized structures; accordingly, while the benchmark tests indicate that the resulting trends in spin-state ordering and relative barrier heights are qualitatively robust, the absolute energies may retain some dependence on the underlying DFT geometries.

For the unsupported Ni system, single-point calculations with multiple local and hybrid functionals (M06L,⁶⁶ M06,⁶¹ PBE,⁶⁷ PBE0,⁶⁸ B3LYP,^{53,54} and dispersion (D3BJ)^{69,70} corrected PBE, PBE0, and B3LYP) were performed on B3LYP-optimized geometries to assess functional dependence. For all remaining systems, including silica-supported models and Fe-based bimetallic hydride analogues, B3LYP functional was used exclusively to maintain consistency across the four systems studied. All DFT calculations were performed in ORCA v6.0.1.^{71,72}

4.2 Multireference calculations

Multireference calculations were performed using the localized active space self-consistent field (LASSCF)⁴³ as implemented in the mrh code⁷³ within PySCF.^{74,75} GPU-accelerated LASSCF⁴⁶ was employed for all calculations, providing speedups of up to 13x with 8 GPUs relative to CPU-only execution (Figure S7). CASSCF calculations were also performed within the same GPU-accelerated version. For the bimetallic Ni systems, the minimal (4,4) active space comprises two unpaired electrons on two 3*d* orbitals of each fragmented Ni (II)(*d*⁸) center. The active space of (16,16) is partitioned as two fragments of (8,8) centered on each Ni center. Each fragment include five 3*d* and three correlating 4*d* orbitals. The number of correlating 4*d* orbitals corresponds to the number of doubly occupied 3*d* orbitals on each metal center: for Ni(II), three of the five 3*d* orbitals are doubly occupied, and each requires a correlating 4*d* orbital to describe the “double-shell” radial correlation effect.⁷⁶ The active space of (16,20) includes all the 4*d* orbitals of each Ni center. For the Fe(II) (*d*⁶) systems, a (8,8) minimal active space consists of four unpaired electrons on four orbitals of each Fe center, (12,12) active space with (6,6) per fragment:

five $3d$ orbitals and one correlating $4d$ orbital corresponding to one doubly occupied $3d$ orbital and (12,20) consists of all $4d$ orbitals.

Inter-fragment correlation is introduced through localized active space state interaction singles (LASSIS),⁴⁷ in which all states generated within the LASSCF fragment decomposition were included in the state interaction. The fragment definitions used in LASSIS were identical to those employed in the LASSCF calculations described above. Dynamical correlations are subsequently incorporated via multiconfiguration pair-density functional theory (MC-PDFT) using three on-top functionals, the translated versions of PBE and PBE0 i.e., tPBE,⁴⁸ tPBE0,⁵⁶ and MC23.⁵⁷

Spin ladders were constructed for all intermediates and transition states by computing the energies of all spin states arising from the coupling of the two metal centers. For the Ni dimer, two $S=1$ centers couple to give open-shell singlet (OSS), triplet (T), and quintet (Q) states. For the Fe dimer, two $S=2$ centers lead to five states, open-shell singlet (OSS), triplet (T), quintet (Q), septet (S), and nonet (N).

The N -diagnostic was evaluated to quantify the degree of multireference character using the natural orbital occupation numbers (NOONs) obtained from LASSCF where N is calculated according to the following equation,⁵⁷

$$N = \frac{1}{2} \left[2 - N_{MCDO MO} + N_{MCU MO} + \sum_i^{n_{SOMO}} |N_{SOMO,i} - 1| \right] \quad (1)$$

$N_{MCDO MO}$ is the NOON of the most correlated nominally doubly occupied molecular orbital, $N_{MCU MO}$ is the NOON of the most correlated nominally unoccupied molecular orbital, and $N_{SOMO,i}$ is the NOON of the i th nominally singly occupied molecular orbital, and n_{SOMO} is the total number of singly occupied molecular orbitals. Following the classification scheme proposed by Bao et al.,⁵⁷ orbitals with NOONs greater than or equal to 1.5 are classified as doubly occupied, those with NOONs less than or equal to 0.5 as unoccupied, and those with NOONs between 0.5 and 1.5 as singly occupied. Mulliken population analysis was performed on the LASSCF wave functions to obtain atomic

charges.⁷⁷

5 Data Availability

The data supporting the findings of this study are available within the paper and its supplementary information file.

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Authors Contribution: R.K. and C.L. conceived the study. R.K. performed all computations under the supervision of C.L. R.K. and C.L. led the manuscript preparation. M.R.H., V.A., C.K., and L.G. contributed to scientific discussions throughout the project, and C.K. also assisted with code installation and debugging. All authors provided critical feedback and helped shape the research, analysis, and manuscript.

Supporting Information Available: MC-PDFT and NEVPT2 comparison of reaction profile, Electronic and Gibbs Energies, Profiling graphs, Spin-state energetics, N-diagnostic,

and Mulliken charges(PDF), and xyz coordinates of all the complexes (ZIP).

Competing Interests: There are no conflicts of interest to declare.

References

- (1) Claus, P. Selective hydrogenation of α , β -unsaturated aldehydes and other C=O and C=C bonds containing compounds. *Top. Catal.* **1998**, *5*, 51–62.
- (2) Chorkendorff, I.; Niemantsverdriet, J. W. *Concepts of modern catalysis and kinetics*; John Wiley & Sons, 2017.
- (3) Hagen, J. *Industrial catalysis: a practical approach*; John Wiley & Sons, 2015.
- (4) Wasim, E.; et al. Ligand-coordination effects on the selective hydrogenation of acetylene in single-site Pd-ligand supported catalysts. *J. Catal.* **2022**, *413*, 81–92.
- (5) Jung, U.; et al. Comparative in operando studies in heterogeneous catalysis: atomic and electronic structural features in the hydrogenation of ethylene over supported Pd and Pt catalysts. *ACS Catal.* **2015**, *5*, 1539–1551.
- (6) Coperet, C.; et al. Surface organometallic and coordination chemistry toward single-site heterogeneous catalysts: strategies, methods, structures, and activities. *Chem. Rev.* **2016**, *116*, 323–421.
- (7) Kanbur, U.; et al. Supported organochromium ethylene oligomerization enabled by surface lithiation. *ACS Catal.* **2024**, *14*, 8640–8651.
- (8) Xu, J.; Lund, C.; Patel, P.; Kim, Y. L.; Liu, C. Recent advances on computational modeling of supported single-atom and cluster catalysts: characterization, catalyst–support interaction, and active site heterogeneity. *Catalysts* **2024**, *14*, 224.
- (9) Kanbur, U.; et al. Supported Electrophilic Organoruthenium Catalyst for the Hydrosilylation of Olefins. *ACS Catal.* **2023**, *13*, 13383–13394.

- (10) Camacho-Bunquin, J.; et al. Chemoselective hydrogenation with supported organoplatinum (IV) catalyst on Zn (II)-modified silica. *J. Am. Chem. Soc.* **2018**, *140*, 3940–3951.
- (11) Kim, Y. L.; et al. Supported Single-Atom Manganese Catalysts for the Trimerization of Ethylene. *ChemCatChem* **2025**, *17*, e00331.
- (12) Sohn, H.; et al. Isolated, well-defined organovanadium (III) on silica: single-site catalyst for hydrogenation of alkenes and alkynes. *Chem. Comm.* **2017**, *53*, 7325–7328.
- (13) Kaphan, D. M.; et al. Mechanistic Aspects of a Surface Organovanadium (III) Catalyst for Hydrocarbon Hydrogenation and Dehydrogenation. *ACS Catal.* **2019**, *9*, 11055–11066.
- (14) Chen, L.; et al. Ligand-coordinated Ir single-atom catalysts stabilized on oxide supports for ethylene hydrogenation and their evolution under a reductive atmosphere. *Catal. Sci. Technol.* **2021**, *11*, 2081–2093.
- (15) Rimoldi, M.; Fodor, D.; van Bokhoven, J. A.; Mezzetti, A. A stable 16-electron iridium (III) hydride complex grafted on SBA-15: a single-site catalyst for alkene hydrogenation. *Chem. Comm.* **2013**, *49*, 11314–11316.
- (16) Scott, S. L.; et al. Silica-supported rhodium hydrides stabilized by triisopropylphosphine. *J. Mol. Catal. A: Chem.* **2003**, *204*, 457–463.
- (17) An, S.; Patel, P.; Liu, C.; Skodje, R. T. Active Site Engineering via Optimizing the Heterogeneous Support Structure for Single-Atom Catalysis. *J. Phys. Chem. C* **2023**, *127*, 16901–16913.
- (18) Wells, R. H.; An, S.; Patel, P.; Liu, C.; Skodje, R. T. Single-molecule kinetics of styrene hydrogenation on silica-supported vanadium: The role of disorder for single-atom catalysts. *J. Phys. Chem. C* **2021**, *125*, 20286–20300.

- (19) Patel, P.; et al. Computational investigation of the role of active site heterogeneity for a supported organovanadium (iii) hydrogenation catalyst. *ACS Catal.* **2021**, *11*, 7257–7269.
- (20) Plascencia, C.; Curtiss, L. A.; Liu, C. Hydrogen activation by silica-supported metal ion catalysts: catalytic properties of metals and performance of DFT functionals. *J. Phys. Chem. A* **2018**, *123*, 171–186.
- (21) Liu, C.; et al. Development of activity–descriptor relationships for supported metal ion hydrogenation catalysts on silica. *Polyhedron* **2018**, *152*, 73–83.
- (22) Czerny, F.; et al. Well-defined, silica-supported homobimetallic nickel hydride hydrogenation catalyst. *Inorg. Chem.* **2021**, *60*, 5483–5487.
- (23) Pfirrmann, S.; Limberg, C.; Ziemer, B. A low-coordinate nickel (ii) hydride complex and its reactivity. *Dalton Trans.* **2008**, 6689–6691.
- (24) Radoń, M. Benchmarks for transition metal spin-state energetics: why and how to employ experimental reference data? *Phys. Chem. Chem. Phys.* **2023**, *25*, 30800–30820.
- (25) Nandy, A.; et al. Large-scale comparison of 3d and 4d transition metal complexes illuminates the reduced effect of exchange on second-row spin-state energetics. *Phys. Chem. Chem. Phys.* **2020**, *22*, 19326–19341.
- (26) Wardzala, J. J.; et al. From Oxo to Oxyl to Biradical: Systematic Multireference Calculations of Methane Activation at MOF Nodes. **2026**, DOI: <https://doi.org/10.26434/chemrxiv.15000688/v1>.
- (27) Ghosh, A. Transition metal spin state energetics and noninnocent systems: challenges for DFT in the bioinorganic arena. *J. Biol. Inorg. Chem.* **2006**, *11*, 712–724.
- (28) Radoń, M. *Adv. Inorg. Chem.*; Elsevier, 2019; Vol. 73; pp 221–264.

- (29) Vogiatzis, K. D.; et al. Computational Approach to Molecular Catalysis by 3d Transition Metals: Challenges and Opportunities. *Chem. Rev.* **2019**, *119*, 2453–2523.
- (30) Mandal, M.; Hermes, M. R.; Berger, F.; Sauer, J.; Gagliardi, L. Modeling Oxidative Dehydrogenation of Propane with Supported Vanadia Catalysts Using Multireference Methods. *J. Phys. Chem. C* **2025**, *129*, 14418–14429.
- (31) Gaggioli, C. A.; Stoneburner, S. J.; Cramer, C. J.; Gagliardi, L. Beyond density functional theory: the multiconfigurational approach to model heterogeneous catalysis. *ACS Catal.* **2019**, *9*, 8481–8502.
- (32) Vitillo, J. G.; Cramer, C. J.; Gagliardi, L. Multireference methods are realistic and useful tools for modeling catalysis. *Isr. J. Chem.* **2022**, *62*, e202100136.
- (33) Khurana, R.; Agarawal, V.; Liu, C. Exploring the Computational Aspects of Propylene Oligomerization Catalysis Using M₂M Type Trimetallic MOF Nodes. *J. Phys. Chem. C* **2024**, *128*, 16986–16995.
- (34) Bernales, V.; et al. Computationally Guided Discovery of a Catalytic Cobalt-Decorated Metal–Organic Framework for Ethylene Dimerization. *J. Phys. Chem. C* **2016**, *120*, 23576–23583.
- (35) Gaggioli, C. A.; Sauer, J.; Gagliardi, L. Hydrogen Atom or Proton Coupled Electron Transfer? C–H Bond Activation by Transition-Metal Oxides. *J. Am. Chem. Soc.* **2019**, *141*, 14603–14611.
- (36) Khan, S. N.; Quebedeaux, B.; Miliordos, E. Selective conversion of methane to methanol facilitated by molecular metal–methoxy complexes via a self-correcting chemical cycle. *Phys. Chem. Chem. Phys.* **2024**, *26*, 23136–23143.
- (37) He, N.; Nakatani, N.; Hada, M. How does multi-reference computation change the catalysis chemistry? DFT and CASPT2 studies of the Cu-catalysed coupling reac-

- tions between aryl iodides and β -diketones. *Phys. Chem. Chem. Phys.* **2023**, *25*, 28871–28884.
- (38) Roos, B. O.; Taylor, P. R.; Sigbahn, P. E. A complete active space SCF method (CASSCF) using a density matrix formulated super-CI approach. *Chem. Phys.* **1980**, *48*, 157–173.
- (39) Malmqvist, P. Å.; Rendell, A.; Roos, B. O. The restricted active space self-consistent-field method, implemented with a split graph unitary group approach. *J. Phys. Chem.* **1990**, *94*, 5477–5482.
- (40) Andersson, K.; Malmqvist, P. A.; Roos, B. O.; Sadlej, A. J.; Wolinski, K. Second-order perturbation theory with a CASSCF reference function. *J. Phys. Chem.* **1990**, *94*, 5483–5488.
- (41) Andersson, K.; Malmqvist, P.-Å.; Roos, B. O. Second-order perturbation theory with a complete active space self-consistent field reference function. *J. Chem. Phys.* **1992**, *96*, 1218–1226.
- (42) Angeli, C.; Cimiraglia, R.; Evangelisti, S.; Leininger, T.; Malrieu, J.-P. Introduction of n-electron valence states for multireference perturbation theory. *J. Chem. Phys.* **2001**, *114*, 10252–10264.
- (43) Hermes, M. R.; Gagliardi, L. Multiconfigurational self-consistent field theory with density matrix embedding: The localized active space self-consistent field method. *J. Chem. Theory Comput.* **2019**, *15*, 972–986.
- (44) Wardzala, J. J.; et al. Multireference Methods for Chemistry and Materials Science: Automated Active Spaces, Efficient Dynamic Correlation, and Extended Systems. *Chem. Rev.* **2026**, *126*, 4592–4618.

- (45) Hermes, M. R.; Pandharkar, R.; Gagliardi, L. Variational localized active space self-consistent field method. *J. Chem. Theory . Computat.* **2020**, *16*, 4923–4937.
- (46) Agarawal, V.; Khurana, R.; Liu, C.; Hermes, M. R.; Knight, C.; Gagliardi, L. Enabling Multireference Calculations on Multimetallic Systems with Graphic Processing Units. *J. Chem. Theory Comput.* **2025**, *21*, 7378–7393.
- (47) Hermes, M. R.; Jangid, B.; Agarawal, V.; Gagliardi, L. Localized active space state interaction singles. *J. Chem. Theory Comput.* **2025**, *21*, 6446–6463.
- (48) Li Manni, G.; et al. Multiconfiguration Pair-Density Functional Theory. *J. Chem. Theory Comput.* **2014**, *10*, 3669–3680.
- (49) Zhou, C.; et al. Electronic structure of strongly correlated systems: recent developments in multiconfiguration pair-density functional theory and multiconfiguration nonclassical-energy functional theory. *Chem. Sci.* **2022**, *13*, 7685–7706.
- (50) Feher, F. J.; Newman, D. A.; Walzer, J. F. Silsesquioxanes as models for silica surfaces. *J. Am. Chem. Soc.* **1989**, *111*, 1741–1748.
- (51) Rimola, A.; Costa, D.; Sodupe, M.; Lambert, J.-F.; Ugliengo, P. Silica surface features and their role in the adsorption of biomolecules: computational modeling and experiments. *Chem. Rev.* **2013**, *113*, 4216–4313.
- (52) Handzlik, J.; Grybos, R.; Tielens, F. Structure of monomeric chromium (VI) oxide species supported on silica: periodic and cluster DFT studies. *J. Phys. Chem. C* **2013**, *117*, 8138–8149.
- (53) Becke, A. D. A new mixing of Hartree–Fock and local density-functional theories. *J. Chem. Phys.* **1993**, *98*, 1372–1377.
- (54) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988**, *37*, 785–789.

- (55) Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.
- (56) Pandharkar, R.; Hermes, M. R.; Truhlar, D. G.; Gagliardi, L. A New Mixing of Nonlocal Exchange and Nonlocal Correlation with Multiconfiguration Pair-Density Functional Theory. *J. Phys. Chem. Lett.* **2020**, *11*, 10158–10163.
- (57) Bao, J. J.; Zhang, D.; Zhang, S.; Gagliardi, L.; Truhlar, D. G. A hybrid meta on-top functional for multiconfiguration pair-density functional theory. *Proc. Natl. Acad. Sci. U. S. A.* **2025**, *122*, e2419413121.
- (58) Allen, B. S.; et al. Aurora: Architecting argonne’s first exascale supercomputer for accelerated scientific discovery. *arXiv preprint* **2025**, arXiv:2509.08207.
- (59) Smith, J. M.; Lachicotte, R. J.; Holland, P. L. NN bond cleavage by a low-coordinate iron (II) hydride complex. *J. Am. Chem. Soc.* **2003**, *125*, 15752–15753.
- (60) Tsipis, A. C. Unveiling the nature of binding interactions of acetylene and ethylene with triangular coinage metal clusters: a DFT computational study. *Organometallics* **2010**, *29*, 354–363.
- (61) Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 215–241.
- (62) Ikeda, A.; Nakao, Y.; Sato, H.; Sakaki, S. Binding energy of Transition-metal complexes with large π -conjugate systems. Density functional theory vs Post-Hartree-Fock methods. *J. Phys. Chem. A* **2007**, *111*, 7124–7132.

- (63) Langeslay, R. R.; et al. Nuclearity effects in supported, single-site Fe (II) hydrogenation pre-catalysts. *Dalton Trans.* **2018**, 47, 10842–10846.
- (64) Stoychev, G. L.; Auer, A. A.; Neese, F. Automatic generation of auxiliary basis sets. *J. Chem. Theory Comput.* **2017**, 13, 554–562.
- (65) Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U. Efficient, approximate and parallel Hartree-Fock and hybrid DFT calculations. A 'chain-of-spheres' algorithm for the Hartree-Fock exchange. *Chem. Phys.* **2009**, 98–109.
- (66) Zhao, Y.; Truhlar, D. G. A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions. *J. Chem. Phys.* **2006**, 125.
- (67) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, 77, 3865.
- (68) Adamo, C.; Cossi, M.; Barone, V. An accurate density functional method for the study of magnetic properties: the PBE0 model. *J. Mol. Struct.: THEOCHEM* **1999**, 493, 145–157.
- (69) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, 132, 154104.
- (70) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **2011**, 32, 1456–1465.
- (71) Neese, F. The ORCA program system. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, 2, 73–78.
- (72) Neese, F. Software Update: The ORCA Program System—Version 6.0. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2025**, 15, e70019.

- (73) Hermes, M. R. <https://github.com/MatthewRHermes/mrh> Commit ID: 49a5950. 2018; <https://github.com/MatthewRHermes/mrh>.
- (74) Sun, Q.; et al. PySCF: the Python-based simulations of chemistry framework. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2018**, *8*, e1340.
- (75) Sun, Q.; et al. Recent developments in the PySCF program package. *J. Chem. Phys.* **2020**, *153*, 024109.
- (76) Roos, B. O.; et al. Multiconfigurational perturbation theory: Applications in electronic spectroscopy. *Advances in chemical physics: new methods in computational quantum mechanics* **1996**, *93*, 219–331.
- (77) Huzinaga, S.; Narita, S. Mulliken population analysis and point charge model of molecules. *Isr. J. Chem.* **1980**, *19*, 242–254.

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