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Quantum Chemical Analysis of Novel Catalysts for Sustainable Industrial Reactions

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ABSTRACT

The transition toward sustainable industrial chemistry depends on catalysts that are efficient, selective, durable and built from earth-abundant elements. This article presents a quantum chemical framework for analysing a family of novel first-row transition metal pincer-type catalysts intended for hydrogenation, carbon dioxide activation and selective oxidation. Using density functional theory with dispersion corrections and implicit solvation, the study examines geometric structure, electronic distribution, frontier orbital behaviour, reaction pathways and energetic span for each candidate. The discussion shows how reactivity descriptors, charge transfer and ligand field effects together explain differences in catalytic performance, and how computed barriers can be linked to industrial operating conditions. The numerical values quoted are representative of the trends typically obtained for this class of systems and are used to illustrate the workflow. The analysis identifies cobalt and iron based scaffolds with strongly donating ligands as the most promising candidates, combining low activation barriers with favourable regeneration energetics. The work argues that systematic quantum chemical screening can shorten catalyst development cycles, reduce experimental waste and support greener industrial practice.

Key words: *Density functional theory, Sustainable catalysis, Transition metal complexes, Reaction mechanism, Green chemistry*

Introduction:

Industrial chemistry underpins fertilisers, fuels, polymers, pharmaceuticals and textiles, yet it is also responsible for a large share of global energy use and carbon emissions. Catalysts lie at the centre of this paradox. A good catalyst lowers the energy needed to drive a reaction, increases selectivity and reduces waste, which is exactly what the principles of green chemistry demand. Many of the most active industrial catalysts, however, rely on scarce and expensive platinum group metals, and their supply chains are fragile. For countries with growing industrial sectors, such as Pakistan, where textile, fertiliser and chemical manufacturing are economically important, the development of low cost and efficient catalysts is both an environmental and an economic priority.

Traditional catalyst discovery depends on repeated synthesis and testing, which is slow, consumes reagents and generates hazardous waste. Quantum chemistry offers a

complementary route. By solving approximate forms of the electronic Schrödinger equation, it is possible to predict structures, energies and reaction pathways before a single compound is prepared. Density functional theory has become the main tool for this purpose because it balances accuracy and computational cost for molecules containing transition metals. Landmark work on computational catalyst design has shown that carefully chosen descriptors can guide experimentalists toward promising materials.

This article develops a quantum chemical analysis of novel catalysts built on earth-abundant metals supported by tridentate pincer ligands. The aim is to explain, at the electronic level, why certain metal and ligand combinations perform better, and to translate those insights into guidance for sustainable industrial reactions. The sections that follow describe the methodology, design strategy, structural and electronic analysis, reactivity descriptors, mechanistic pathways, kinetic evaluation, environmental effects, industrial relevance and current limitations.

1. Computational Methodology and Theoretical Framework

All calculations in this type of study are carried out within Kohn–Sham density functional theory. Geometry optimisations are performed with a hybrid functional such as B3LYP, which mixes exact exchange with gradient-corrected exchange and correlation, and which remains widely used for organometallic systems. Because transition metal energetics can be sensitive to the functional, single-point energies are refined with a meta-hybrid functional from the Minnesota family, and results are compared to confirm that conclusions do not depend on one particular choice.

Basis sets of triple-zeta quality with polarisation functions are employed for all atoms, with effective core potentials reserved for heavier elements when required. Long-range dispersion interactions, which strongly influence substrate binding and ligand conformation, are included through the empirical D3 correction with Becke–Johnson damping. Solvent effects are treated with a continuum model based on solute electron density, allowing the polarity of industrial solvents to be mimicked without the cost of explicit molecules.

Every stationary point is characterised by a vibrational frequency calculation. Minima must have no imaginary frequencies, while transition states must have exactly one, and intrinsic reaction coordinate paths are followed to confirm that each transition state connects the intended reactant and product. Thermal corrections give

enthalpies and free energies at the operating temperature, and quasi-harmonic treatments reduce errors from low-frequency modes. Programs such as ORCA and Gaussian are suitable for carrying out this workflow.

2. Design Strategy for Novel Catalysts

The design strategy begins with the choice of metal. Iron, cobalt, nickel, copper and manganese are abundant, inexpensive and display rich redox chemistry, making them attractive replacements for noble metals. Each metal offers different d-electron counts and spin states, so the study treats spin as a variable rather than an assumption, comparing low, intermediate and high spin surfaces for every intermediate.

The second design element is the ligand. Pincer frameworks bind a metal through three donor atoms in a meridional arrangement, giving thermal stability and a well-defined coordination pocket. By varying the donor atoms, for example phosphorus, nitrogen or carbene carbon, and by adding electron-donating or electron-withdrawing substituents on the backbone, the electronic character of the metal centre can be tuned smoothly. Some designs also include a cooperative site on the ligand that can accept or donate a proton, allowing metal–ligand cooperation in bond activation steps.

Candidate structures are generated in a small library and screened in stages. A fast screen using simple descriptors removes poor candidates, and only the best performers proceed to full mechanistic analysis. This tiered approach keeps computational cost manageable while preserving the chance of finding unexpected leaders.

3. Geometric and Electronic Structure Analysis

Optimised geometries reveal how the ligand environment shapes the metal centre. In the model series, five-coordinate cobalt and iron complexes adopt distorted square-pyramidal arrangements, while nickel prefers square-planar geometry. Metal–ligand bond lengths shorten as donor strength increases, and the trans influence of strongly donating groups lengthens the bond opposite to them, which is often the site where a substrate binds.

Natural population analysis provides atomic charges and orbital occupations that go beyond simple oxidation state labels. In strongly donating ligand environments, the metal carries a less positive charge than formal counting suggests, because electron density flows from the ligand into metal d and s orbitals. This partial charge neutralisation is important for reactions that require the metal to act as an electron donor, such as oxidative addition of hydrogen.

Spin density maps show whether unpaired electrons are localised on the

metal or delocalised onto the ligand. When the ligand is redox active, it can store electrons temporarily and relieve the metal of extreme oxidation states. This behaviour explains why some first-row complexes can perform multi-electron transformations that were once thought to require precious metals.

4. Frontier Molecular Orbital and Reactivity Descriptors

Frontier molecular orbital theory links electronic structure to chemical behaviour. The highest occupied molecular orbital reflects electron-donating ability, while the lowest unoccupied molecular orbital reflects electron-accepting ability, and the gap between them is a measure of kinetic stability and polarisability. In the model series, catalysts with smaller gaps bind substrates more strongly but risk over-stabilising intermediates, which can slow turnover.

Conceptual density functional theory supplies quantitative descriptors derived from these orbital energies. Chemical hardness and softness describe resistance to charge redistribution, chemical potential indicates the tendency of electrons to escape, and the electrophilicity index measures the energy stabilisation gained when a species accepts electrons. Local descriptors such as Fukui functions identify which atoms are most likely to take part in nucleophilic or electrophilic attack.

These descriptors are most useful when correlated with computed barriers. For the screened series, a moderate electrophilicity index paired with a medium orbital gap tracks with the lowest activation energies, supporting the Sabatier principle that the best catalyst binds intermediates neither too weakly nor too strongly. Such correlations allow rapid prediction of performance for new ligands without repeating full mechanistic studies.

5. Reaction Mechanism and Potential Energy Surfaces

The mechanism is explored by mapping the potential energy surface for the full catalytic cycle. For hydrogenation, the cycle includes substrate coordination, activation of molecular hydrogen, hydride transfer to the substrate, product release and regeneration of the active species. For carbon dioxide activation, the key steps are coordination of the molecule, formation of a metal–carboxylate or formate species, and hydride or proton delivery. Selective oxidation follows a different pattern, involving formation of a high-valent metal–oxo intermediate that transfers oxygen to the substrate.

Transition states are located for each elementary step, and competing pathways are examined side by side. In the model cobalt system, hydrogen

splitting occurs through a metal–ligand cooperative route in which the metal accepts a hydride while a basic site on the ligand accepts a proton. This pathway has a noticeably lower barrier than a purely metal-centred oxidative addition, illustrating the advantage of cooperative design.

Spin crossing is treated carefully. In several iron and manganese intermediates, low and high spin surfaces lie close in energy, and the reaction can switch surfaces near the transition region. This two-state reactivity can lower the effective barrier and must be included to avoid overestimating activation energies.

6. Kinetic and Thermodynamic Evaluation

Thermodynamic evaluation checks that each step of the cycle is feasible under practical conditions. Reaction free energies reveal whether intermediates are stable enough to form but not so stable that they become resting states trapping the catalyst. The overall reaction energy must of course be favourable, but the profile of the individual steps determines the speed of turnover.

The energetic span model converts a full free energy profile into a single quantity that controls turnover frequency. It identifies the turnover determining transition state and the turnover determining intermediate, and the difference between their energies gives the effective barrier of the entire cycle. Unlike a simple rate-limiting step analysis, it accounts for the whole profile and for the effect of reactant concentrations.

7. Solvent and Dispersion Effects

Industrial reactions seldom occur in the gas phase, and solvent can change both the energies and the preferred pathway. Continuum solvation lowers the energy of charged and polar species, stabilising ionic intermediates and transition states with charge separation. In the model hydrogenation cycle, moving from a nonpolar to a polar medium reduces the barrier of heterolytic hydrogen splitting, which involves partial charge development.

Dispersion corrections are equally important. Bulky substituents on the ligand frame create attractive van der Waals contacts with the substrate, and neglecting them can overestimate barriers by several kilojoules per mole. At the same time, steric crowding can block substrate approach, so dispersion and repulsion must be balanced. Comparison of calculations with and without dispersion corrections shows that selectivity between competing substrates can change, a result with direct consequences for industrial product distributions.

Where specific interactions such as hydrogen bonding with protic solvents

are expected, a few explicit solvent molecules can be added to the continuum model. This hybrid treatment captures local effects while remaining affordable, and it should be used whenever proton transfer steps are central to the mechanism.

8. Sustainability and Industrial Applicability

A catalyst is only sustainable if its entire life cycle is considered. The computational study therefore connects its findings to green chemistry metrics. Replacing platinum group metals with iron or cobalt lowers raw material cost and reduces mining impact. High turnover numbers predicted from small energetic spans imply lower catalyst loading, less metal waste and easier product purification. Selective catalysts also reduce by-products, improving atom economy and lowering the energy needed for separation.

Industrial relevance extends to specific sectors. Hydrogenation catalysts support production of pharmaceuticals and fine chemicals, carbon dioxide activation catalysts offer routes to formate and methanol, and selective oxidation catalysts can replace stoichiometric oxidants that generate hazardous waste in textile and chemical processing. Computed stability against ligand degradation, assessed through bond dissociation energies and decomposition pathways, indicates whether a catalyst can survive prolonged operation at elevated temperature.

For developing industrial economies, computational screening is particularly valuable. It requires modest hardware compared with a fully equipped synthetic laboratory, allows local researchers to focus experimental effort on the few best candidates and supports national goals for cleaner production. Partnerships between universities and industry can turn such predictions into pilot-scale trials.

9. Limitations and Future Perspectives

Despite its power, quantum chemical modelling has limits. Density functional approximations can show errors of several kilocalories per mole for transition metal spin state energetics, and this level of uncertainty can change the ranking of closely matched catalysts. Higher-level methods, such as domain-based local coupled cluster approaches, can benchmark key points, but their cost restricts use to small model systems.

Models of isolated molecules also ignore factors that matter in practice, including catalyst aggregation, deactivation by impurities, mass transport and surface effects when complexes are anchored to supports. Bridging this gap will require multiscale strategies that couple quantum chemistry with microkinetic modelling and, where relevant, molecular dynamics.

The future lies in combining electronic structure calculations with machine learning. Models trained on large databases of computed barriers and descriptors can predict performance in seconds, guiding automated exploration of vast chemical spaces. Experimental validation will remain essential, and a close loop between calculation, synthesis and testing offers the fastest path to catalysts that are both high performing and environmentally responsible.

Summary

This article presented a quantum chemical approach to the analysis of novel earth-abundant catalysts for sustainable industrial reactions. Density functional theory with dispersion and solvation corrections provides a reliable framework for studying structure, bonding and reactivity. Ligand design, spin state accessibility and metal–ligand cooperation emerged as the main factors controlling catalytic performance. Frontier orbital analysis and conceptual density functional descriptors correlate with computed barriers and offer fast screening tools, while the energetic span model links the full reaction profile to turnover frequency. Cobalt and iron pincer systems with strongly donating ligands were identified as the most promising candidates in the illustrative series. Considerations of solvent, dispersion, stability and green chemistry metrics connect the calculations to industrial practice, and the discussion of limitations highlights the need for benchmarking, multiscale modelling and experimental validation. Overall, computational screening can accelerate the discovery of efficient, low cost and environmentally friendly catalysts.

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