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A comprehensive review of Nano-catalysis for green chemistry and its applications

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Abstract

Nano-catalysis has emerged as a transformative approach in green chemistry, offering enhanced reaction efficiency, selectivity, and sustainability. This review explores the principles of nano-catalysis, its role in promoting environmentally benign chemical processes, and its diverse applications across organic synthesis, environmental remediation, energy conversion, and biomedical fields. Emphasis is placed on the design of heterogeneous nano-catalysts, their mechanistic advantages, and recent advancements in catalyst engineering. The paper also discusses challenges related to toxicity, recovery, and scalability, while highlighting future directions for sustainable nano-catalytic technologies. Nanocatalysis catalysis performed by materials with at least one nanoscale dimension—has emerged as a central pillar of green chemistry, enabling higher activity, selectivity, and recyclability while lowering energy and material footprints. This review synthesizes concepts, materials, preparation routes, structure–property relationships, mechanistic paradigms, and deployment pathways that make nanocatalysts compelling for sustainable synthesis and environmental remediation. We consolidate recent advances across metal, metal-oxide, carbonaceous, framework (MOF/COF), perovskite, and enzyme–nano hybrids; compare green metrics (atom economy, E-factor, process mass intensity, energy intensity, solvent footprint); survey enabling reactors and process intensification; and critically assess techno-economic viability, life-cycle impacts, and nanosafety. We close with a forward look on circular manufacturing of nanocatalysts, digital design (DFT + ML), and integration with electrification and renewable photons/electrons.

Keywords: Nanocatalysis, green chemistry, heterogeneous catalysis, photocatalysis, electrocatalysis, MOF, COF, carbon nitride, biomass valorization, CO_2 utilization, wastewater remediation

Introduction

Green chemistry seeks to prevent pollution at the source by redesigning molecules, materials, and processes. Catalysis sits at its core, and nanoscale catalysts offer unique leverage: high surface-to-volume ratios, quantum size effects, abundant low-coordination sites, tunable electronic structures, and engineered interfaces. These attributes can (i) reduce precious-metal loading, (ii) enable milder conditions, (iii) increase turnover numbers (TON) and frequencies (TOF), and (iv) facilitate separability and reuse, collectively shrinking waste and energy footprints. Beyond activity, nanostructuring unlocks orthogonal selectivity (e.g., facet/defect control) and cascade reactions via multifunctional interfaces. Green chemistry aims to design chemical processes and products that reduce or eliminate hazardous substances, minimize energy consumption, and promote atom economy. Catalysis is central to this mission, and nano-catalysis—catalysis using nanoparticles—has revolutionized the field by offering superior surface area, tunable reactivity, and enhanced selectivity. Nanoparticles (NPs), due to their quantum size effects and high surface-to-volume ratios, enable reactions under milder conditions with reduced waste and improved yields.

Fundamentals of Nano-Catalysis

Nano-catalysts operate at the interface of nanoscience and catalysis. Their unique properties include:

High surface area: More active sites per unit mass.
Quantum effects: Altered electronic structures enhance reactivity.
Shape and size control: Enables selective activation of substrates.
Support interactions: Anchoring on porous materials improves stability and recyclability.

Catalysts can be classified as
Homogeneous nano-catalysts: Soluble NPs in reaction media.
Heterogeneous nano-catalysts: Immobilized NPs on solid supports, preferred for green chemistry due to ease of separation and reuse.

Nano-Catalysis in Green Organic Synthesis

Nano-catalysts have enabled eco-friendly synthesis of complex molecules
Multi-component reactions (MCRs): Efficient synthesis of imidazoles, coumarins, and pyrazoles using metal oxide NPs.
Solvent-free reactions: Catalyzed by Fe_3O_4, ZnO, and TiO_2 NPs.
Biodegradable supports: Chitosan, cellulose, and silica-based nanocomposites enhance sustainability.
These systems reduce reaction time, eliminate toxic solvents, and improve atom economy.

Environmental Applications

Nano-catalysis plays a pivotal role in environmental remediation**:**
Photocatalytic degradation: TiO_2 and ZnO NPs degrade organic pollutants under UV/visible light.
Heavy metal removal: Functionalized NPs adsorb and reduce toxic ions like Cr(VI), Pb(II), and Hg(II).
Wastewater treatment: Nano-structured catalysts facilitate oxidation of dyes and pharmaceuticals.
These applications align with green chemistry principles by minimizing secondary pollution and energy input.

Energy Conversion and Storage

Nano-catalysts contribute to clean energy technologies

Hydrogen production: Water splitting using Pt, Ru, and Co-based NPs.

Fuel cells: Nanostructured catalysts improve oxygen reduction and methanol oxidation.

CO_2 conversion: Cu and Ni NPs catalyze electrochemical reduction to fuels.

These innovations support decarbonization and sustainable energy systems.

Biomedical and Industrial Applications

In life sciences and industry, nano-catalysis enables**:**

Drug synthesis: Selective transformations with minimal by-products.

Bio-sensors: Catalytic NPs enhance signal detection.

Food processing: Enzyme-mimetic nano-catalysts improve safety and efficiency.

Biocompatible and biodegradable nano-catalysts are being developed to address toxicity concerns.

Scope and Methodological Notes

This narrative review integrates foundational principles and cross-sector case studies spanning fine chemicals, pharmaceuticals, agro-intermediates, polymers, fuels, and water treatment. We emphasize**:** (1) materials classes and green syntheses, (2) mechanistic/kinetic insights relevant to sustainability, (3) process-level integration, and (4) environmental health and safety (EHS) considerations. Tables summarize practical guidance and decision criteria for deployment.

3. Fundamentals of Nanocatalysis

Structure–function: Activity and selectivity scale with accessible active sites, electronic structure, and local fields at interfaces. Size, shape, and support dictate adsorption energies (Sabatier optimum) and reaction pathways.

Heterogeneous vs homogeneous behavior

"Nanocolloids" may behave quasi-homogeneously; leaching/redeposition ("release and catch") can masquerade as heterogeneous turnover. Rigorous hot-filtration, three-phase tests, and poisoning protocols are essential.

Green-relevant kinetics

Lower apparent activation energies and enhanced mass/heat transfer at nanoscale shorten residence times and enable low-temperature operation—critical for reducing energy intensity and side products.

Materials Landscape

1. **Metals and Alloys**

Pt, Pd, Ru, Ni, Cu, and Au nanoparticles; bimetallics (e.g., Pd–Cu, Ni–Fe) and high-entropy alloys. Advantages**:** tunable binding energies via alloying/strain; drawbacks**:** scarcity (PGMs), sintering, and leaching.

2. **Metal Oxides and Mixed Oxides**

CeO_2, TiO_2, ZnO, Fe_3O_4, perovskites (ABO_3), spinels. Offer redox oxygen mobility, acid–base bifunctionality, and (photo)activity. Magnetic oxides (Fe_3O_4) enable facile recovery.

3. **Carbonaceous Catalysts**

Graphene, CNTs, biomass-derived carbons, N-doped carbon, and graphitic carbon nitride (g-C_3N_4). Features**:** metal-free active sites (pyridinic-N, defects), photoredox capability (g-C_3N_4), corrosion resistance, and sustainability via bio-precursors.

4. **Porous Frameworks**

MOFs (UiO-66, MIL, ZIF) and COFs provide uniform active sites, high surface areas, and modularity; function as catalysts, supports, or precursors to M–N–C single-atom catalysts after pyrolysis.

5. **Enzyme–Nano Hybrids**

Immobilized enzymes on magnetic or porous nano-supports; hybrid chemo-/biocatalysis; improved stability, reusability, and solvent tolerance for green media.

Green Synthesis of Nanocatalysts

Benign solvents: water, ethanol, glycerol, deep eutectic solvents (DES), supercritical CO_2.

Reductants/stabilizers from biomass: plant polyphenols, sugars, amino acids; polymer capping with cellulose, chitosan.

Energy-efficient routes: microwave, flow synthesis, mechanochemistry, photochemical reduction.

Circular feedstocks: upcycled metals from e-waste or industrial streams; template-free morphology control to minimize waste.

Design for recycle: magnetic cores, robust supports (ceria, zirconia, N-doped carbon) and sinter-resistant architectures (yolk–shell).

Characterization and Mechanistic Probes

Morphology/structure: TEM/HR-TEM, SEM, AFM, XRD, BET porosimetry.

Surface/electronic state: XPS, UPS, EPR, in situ/operando XAS (XANES/EXAFS), DRIFTS/Raman, ambient-pressure XPS.

Composition/leaching: ICP-OES/MS, elemental analysis, hot-filtration tests.

Kinetics: turnover metrics (TOF, TON), Arrhenius/ERT analysis, microkinetic modeling; isotopic labeling to resolve pathways.

Green metrics alignment: parallel measurement of E-factor, PMI, solvent and energy intensity during screening.

Applications in Green Chemistry

1. **Oxidation under Benign Oxidants**

H_2O_2 and O_2 activation: Au/TiO_2, Pd–Au, and Fe-N-C catalysts for alcohol to aldehyde/ketone; Mn/Fe oxides for selective C–H oxidation; photocatalytic aerobic oxidations on TiO_2/g-C_3N_4 under visible light.

2. **Selective Hydrogenation and Reductive Transformations**

Ni, Cu, and Ru nanocatalysts for nitro-to-amine, biomass-derived platform molecules (furfural/HMF → furfuryl alcohol, BHMF), and chemoselective alkene/alkyne hydrogenations; transfer hydrogenation using formic acid or alcohols in place of H_2.

3. **C–C and C–X Couplings (Low-Pd or Pd-free)**

Pd/C, Pd@MOF, and single-atom Pd for Suzuki–Miyaura under aqueous/ethanol media; Cu-based nano-systems for Ullmann; Ni catalysts for cross-electrophile coupling—lower Pd loading and greener solvents.

4. Photocatalysis and Photo-Redox

g-C_3N_4, TiO_2, doped perovskites, and MOF-derived semiconductors for dye degradation, selective oxidations, and solar-driven H_2 evolution; heterojunctions (g-C_3N_4/TiO_2, MOF/CQDs) to suppress recombination.

5. Electrocatalysis (Power-to-Chemicals)

CO_2 reduction (Cu-based, M–N–C single atoms) to CO, formate, C_2 products; nitrate to ammonia; paired electrolysis to merge oxidation and reduction value chains. Integration with renewable electricity aligns with decarbonization.

6. Biomass Valorization

Acid/base bifunctional oxides and sulfonated carbons for esterification/etherification; metal–acid tandem sites (Ru/C + solid acid) for levulinic acid to γ-valerolactone; Ni–Cu for hydrogenolysis of lignin fragments.

7. Environmental Remediation

Fenton-like magnetite and doped oxides for advanced oxidation processes; photocatalytic degradation of pharmaceuticals; immobilized nano-Ag/Cu_2O with controlled release for antimicrobial coatings in water disinfection.

8. Reactor and Process Intensification

Flow chemistry: packed/structured beds with nano-coatings mitigate mass-transfer limits and hot spots; enhanced safety for exothermic oxidations/hydrogenations; easy scale-out.

Membrane reactors: in situ product separation; catalyst retention for colloidal systems.

Microreactors and photochemical flow: high surface-to-volume, uniform irradiation, fast screening.

Magnetic separation: Fe_3O_4-based catalysts enable rapid decantation and closed-loop reuse.

Solvent minimization: reactive distillation, gas–solid or neat processes when feasible.

9. Measuring "Green": Metrics and Decision Tools

Table 1: Practical Green Metrics for Nanocatalytic Processes

Metric	What it captures	Typical target / note
Atom economy	Stoichiometric efficiency	Design at synthesis stage
E-factor	Mass of waste per mass product	≤ 5 fine chemicals; ≤ 25 pharma (aspirational lower)
PMI	Total mass in per mass product	Complements E-factor; count water/solvents
Energy intensity	kWh per kg product	Lower via low-T catalysis and intensification
Catalyst productivity	TON/TOF over life	Track across regenerations
Recycle index	Performance retention (%)	≥ 90% over ≥ 5 cycles desirable
Solvent score	Toxicity, volatility, recyclability	Favor water, alcohols, esters, Cyrene®, supercritical CO_2

10. Stability, Deactivation, and Regeneration

Modes: sintering (Ostwald ripening), coking, poisoning (S, Cl, P), phase transformation, metal leaching.

Mitigation: alloying/anchoring to strong supports (defect-rich N-doped carbon, Zr-based MOFs), core–shell/yolk–shell designs, oxidative/solvent regenerations, and process controls (impurity management, redox cycling).

Diagnostics: operando XAS/XPS/DRIFTS to correlate degradation with conditions and redesign countermeasures.

11. Techno-Economic Analysis (TEA) and Life-Cycle Assessment (LCA)

Cost drivers: metal loading and recovery, support synthesis, energy input, solvent use, reactor complexity.

Levers: precious-metal minimization via single-atom catalysts or base-metal substitution; flow intensification to reduce CapEx; catalyst lifetime extension; solvent recycle.

LCA lens: include cradle-to-gate impacts of catalyst manufacture (e.g., MOF ligand footprint), and end-of-life recovery (magnetic or leach-re-deposit). Circularity plans should be integral, not afterthoughts.

12. Environmental Health & Safety (EHS) and Regulation

Nanoparticle hazards hinge on composition, size, shape, coating, and solubility. Implement a "safety by design" approach**:** choose benign supports, minimize free nanoparticles (immobilize/encapsulate), quantify release, and maintain exposure controls (closed systems, proper PPE, HEPA capture). Track evolving guidance on nano-materials labeling, waste classification, and worker exposure limits.

13. Case Snapshots (Representative)

Aqueous Suzuki–Miyaura with ppm Pd: Polymer-stabilized Pd clusters or single-atom Pd on N-doped carbon deliver high TON at room temperature in ethanol/water, enabling easy downstream.

Magnetite Fenton-like AOP: Fe_3O_4@carbon composites activate H_2O_2 under visible light at neutral pH for pharmaceutical residue removal; magnetic retrieval supports repeated reuse with minimal iron leaching.

g-C_3N_4 heterojunctions: Z-scheme g-C_3N_4/TiO_2 drives aerobic oxidation of alcohols under LEDs, sidestepping stoichiometric oxidants.

Ni–Cu bimetal for furfural hydrogenation: Base-metal alloying achieves noble-metal-like selectivity with superior cost and LCA profiles.

14. Common Pitfalls and How to Avoid Them

Table 2: Pitfalls Checklist

Pitfall	Risk	Prevention
Apparent heterogeneity hides homogeneous leaching	Misassigned mechanism, fouling	Hot-filtration, three-phase test, ICP of filtrates
Unreported solvent/energy burdens	Green claims collapse in LCA	Always report PMI/E-factor/energy
Catalyst “recyclability” without constant mass/activity basis	Misleading stability	Normalize to TOF, mass balance metals, report selectivity drift
Unsupported claims of “metal-free” activity	Hidden metal contamination	Use metal cavengers/controls; ICP blanks
Scale-up ignores heat/mass transfer	Runaway or poor selectivity	Do pilot flow studies; monitor ΔT, pressure drop

15. Outlook: Where Nanocatalysis Meets the Next Wave of Green Chemistry

Electrification & power-to-X: Marry nanocatalysts with renewables in electro/photocatalytic platforms; pursue paired reactions and co-electrolyte valorization.

Digital design: Integrate DFT-derived descriptors and machine learning for inverse design of compositions, facets, and supports; active learning in flow accelerates optimization.

Single-atom and cluster catalysis: Maximize metal efficiency while engineering neighbor environments for bifunctional mechanisms.

Circular manufacturing: Bio-templating, low-temperature synthesis, and metal recovery loops to shrink catalyst cradle impacts.

Process–catalyst co-design: Co-optimize catalyst with reactor, solvent, separations, and heat integration from day one.

Conclusions

Nanocatalysis offers concrete, near-term routes to greener chemistry**:** higher productivity at lower temperature/pressure, benign oxidants/reductants, recyclable media, and compact intensified reactors. Real sustainability gains, however, require treating catalysts as one component of an integrated, measured process—designed for circularity, verified by metrics, and validated under realistic manufacturing constraints. With rigorous mechanistic understanding, smart materials, and process intensification, nanocatalysis can underpin the next generation of clean syntheses and environmental technologies.

Nomenclature and Abbreviations

AOP, advanced oxidation process; COF, covalent organic framework; DES, deep eutectic solvent; DFT, density functional theory; DRIFTS, diffuse reflectance infrared Fourier transform spectroscopy; EHS, environmental health & safety; EXAFS, extended X-ray absorption fine structure; g-C_3N_4, graphitic carbon nitride; LCA, life-cycle assessment; MOF, metal-organic framework; PMI, process mass intensity; PGM, platinum-group metal; TOF/TON, turnover frequency/number; XANES, X-ray absorption near edge structure; XPS, X-ray photoelectron spectroscopy.

(Optional) Structured Elements You Can Paste Into the Paper

Table 3: Nanocatalyst Class vs. Green Use-Case (quick design guide)

Class	Best for	Typical solvent	Recycle mode
Pd/Ni/Cu NPs (alloyed)	Couplings, hydrogenations	EtOH/H_2O, PEG-400	Filtration; magnetic if core-shell
Fe/Mn/Co oxides	Benign oxidations, AOP	H_2O	Magnetic separation or filtration
g-C_3N_4 & heterojunctions	Photoredox oxidations/reductions	H_2O/MeCN (minimized)	Filtration; stable under light
MOF/COF & derivatives	Size-/site-selective catalysis	EtOH/H_2O	Reuse as packed bed
Enzyme–nano hybrids	Kinetic/enantioselective steps	Aqueous or green biphasic	Magnet or membrane retention

Box 1. Reporting Checklist (for reproducible green nanocatalysis)

Full catalyst synthesis with mass balances and solvent accounting
Surface area, particle size distribution, metal dispersion, and oxidation state
TOF/TON, selectivity, and confidence intervals; deactivation rates
Green metrics (E-factor/PMI/energy); solvent recovery fraction
Recycle tests with ICP of filtrates and activity/selectivity retention
Safety/EHS notes and waste handling

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