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Porous-Supported Transition-Metal Heterogeneous Catalysts for Selective Alcohol Oxidation: A Review of Catalyst Design, Advanced Characterization, Structure–Activity Relationships, and Sustainable Process Development

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Abstract : *Selective oxidation of alcohols to aldehydes and ketones is a crucial transformation in the fine chemical, pharmaceutical, fragrance, agrochemical, and biomass refining value chains. Replacing stoichiometric Cr(VI), Mn(VII), and halogen-based oxidants with recyclable heterogeneous catalysts and benign oxidants is therefore an important objective of sustainable catalysis. This review focuses specifically on non-noble transition-metal catalysts immobilized on porous inorganic supports, with emphasis on Cu, Mn, Co, Fe, Ni, and V in monometallic and bimetallic forms. Alumina, conventional zeolites, ZSM-5, ZSM-22, SBA-15, and MCM-41 are discussed as chemically active supports rather than inert carriers. Their pore dimensions, acidity, hydroxyl density, metal-support interaction, and diffusion environment regulate metal dispersion, oxidation state, oxygen activation, and suppression of over-oxidation. Representative systems illustrate how isolated ions, oxide nanodomains, and mixed-metal interfaces can promote selective dehydrogenation/oxidation with O_2, air, H_2O_2, or tert-butyl hydroperoxide. Particular attention is given to advanced characterization by XRD, N_2 physisorption, electron microscopy, XPS, UV-Vis/DRS, Raman, FTIR, H_2-TPR, O_2-TPD, NH_3-TPD, pyridine-FTIR, ICP-OES, and operando methods, and to the structure-activity descriptors obtained from these techniques. The review further evaluates bimetallic synergy, oxygen vacancies, redox-acid cooperation, pore confinement, catalyst stability, and leaching. Finally, design rules and research priorities are proposed for translating porous-supported earth-abundant metal catalysts toward solvent-minimized, continuous, and industrially credible alcohol oxidation processes.*

Key Words: heterogeneous catalysis, non-noble transition metals, bimetallic catalysts, catalyst characterization, structure-activity relationship.

I. INTRODUCTION

The controlled oxidation of primary and secondary alcohols provides aldehydes and ketones that are indispensable intermediates for fine chemicals, flavors, fragrances, pharmaceuticals, polymers, and biomass-derived products. Classical laboratory oxidants can deliver high yields, but their stoichiometric use produces inorganic waste and complicates product purification. Heterogeneous oxidation using molecular oxygen, air, or hydrogen peroxide offers a

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more attractive route because the catalyst can be separated, reused, and potentially implemented in fixed-bed or continuous-flow reactors [1-5]. The challenge is selectivity: aldehydes are readily over-oxidized to acids, while aromatic alcohols can undergo C-C cleavage, condensation, or complete oxidation if the catalyst contains excessively strong redox or acid sites.

Noble metals such as Au, Pd, Pt, and Ru have dominated much of the high-performance literature, yet cost, supply risk, and sensitivity to poisons motivate the development of earth-abundant alternatives. Cu, Mn, Co, Fe, Ni, and V are especially relevant because they access multiple oxidation states and can activate O_2 or peroxides through redox cycles. Their performance changes profoundly when they are dispersed inside or on porous oxides. A porous support controls particle size, local coordination, metal-support charge transfer, acid-base properties, water adsorption, and molecular transport. Consequently, the same metal can behave very differently on gamma-Al_2O_3, SBA-15, MCM-41, or a microporous zeolite [6-10].

This article is deliberately restricted to heterogeneous, non-noble transition-metal systems. Homogeneous molecular catalysts are mentioned only where immobilization or encapsulation establishes a genuine solid catalyst. Particular emphasis is placed on monometallic and bimetallic Cu-, Mn-, Co-, Fe-, Ni-, and V-based materials supported by alumina, zeolites, ZSM-5, ZSM-22, SBA-15, and MCM-41. ZSM-22 is included as an important one-dimensional medium-pore platform whose direct use in selective alcohol oxidation remains much less developed than ZSM-5 or MCM-41; this scarcity itself defines a useful research opportunity.

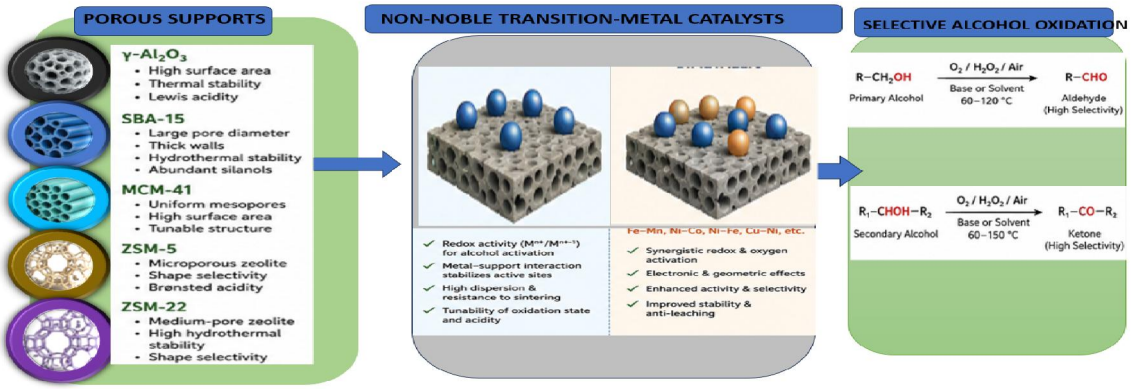


Fig. 1 Porous-Supported Non-Noble Transition-Metal Catalysts for Selective Alcohol Oxidation.

1.1 Significance of Heterogeneous Catalysis over Homogeneous Catalysis

Homogeneous transition-metal catalysts can provide high intrinsic activity and molecular-level control because their active sites are uniformly accessible; however, practical alcohol oxidation often requires difficult catalyst-product separation, generates metal-contaminated product streams, and complicates catalyst recovery and reuse. Heterogeneous catalysts overcome many of these limitations by immobilizing the active transition-metal species on a recoverable solid phase. More importantly, porous supports do not act merely as inert carriers. Gamma-Al_2O_3, SBA-15, MCM-41, ZSM-5, ZSM-22, and other zeolites can regulate metal dispersion, oxidation state, acid-base character, oxygen activation, substrate adsorption, and product residence time through metal-support interactions and confinement. Their high surface areas can stabilize isolated ions or small oxide domains, while controlled pore dimensions can suppress aggregation and, in favorable cases, reduce over-oxidation by facilitating carbonyl-product desorption. Solid catalysts also enable filtration, recycling, and integration into fixed-bed or continuous-flow reactors, which is advantageous for scale-up and reduction of downstream purification. The trade-off is that heterogeneous systems may exhibit site heterogeneity, pore-diffusion resistance, and external mass-transfer limitations. Consequently, effective heterogeneous catalyst design requires simultaneous optimization of metal speciation, pore accessibility, interfacial chemistry, and

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transport. The objective is therefore not simply to replace a soluble catalyst with a solid but to exploit the porous solid to create a more recoverable, stable, and selectively engineered catalytic microenvironment [1-10].

II. CATALYTIC REQUIREMENTS AND REACTION CHEMISTRY

Selective oxidation formally removes two hydrogen atoms from an alcohol. On a redox catalyst, alcohol adsorption is followed by O-H activation to form a surface alkoxide, alpha-C-H cleavage, carbonyl desorption, and reoxidation of the reduced catalyst by the terminal oxidant. In Mars-van Krevelen-type pathways, lattice oxygen participates directly, and the resulting vacancy is replenished by gaseous O_2. In peroxide routes, surface metal centers generate metal-peroxo, hydroperoxo, or radical-like species. The optimum catalyst must activate the alcohol and oxidant rapidly while releasing the aldehyde or ketone before secondary oxidation occurs [1, 2, 11].

For primary aromatic alcohols, benzyl alcohol to benzaldehyde is the most widely used probe reaction because conversion and selectivity respond sensitively to metal valence, oxygen mobility, and support acidity. Secondary alcohols generally give ketones and are less susceptible to over-oxidation. Aliphatic primary alcohols are more difficult because C-H activation is less favored and diffusion or competitive water adsorption can become important. Therefore, catalyst claims based only on benzyl alcohol should be supported by substrate-scope tests including electron-rich/electron-poor benzyl alcohols, heteroaromatic alcohols such as furfuryl alcohol, and representative aliphatic or secondary alcohols.

III. POROUS SUPPORTS AS ACTIVE DESIGN ELEMENTS

3.1 Gamma-Al_2O_3

Gamma-alumina combines high surface area, thermal stability, hydroxyl-rich anchoring sites, and Lewis acidity. These features stabilize highly dispersed transition-metal oxides, but strong metal-support interaction can either enhance dispersion or make reduction difficult. Mn/gamma-Al_2O_3 is a useful example: potassium promotion changes the supported manganese oxide structure toward more active alpha-MnO_2-like domains and improves aerobic oxidation of aromatic alcohols [12]. Alumina is particularly attractive for gas-phase processing because it tolerates elevated temperature and shaped-body preparation. Its disadvantages are a broad distribution of acid sites and less uniform pore architecture than ordered mesoporous silica.

3.2 Zeolites, ZSM-5, and ZSM-22

Crystalline zeolites offer molecularly defined micropores, ion-exchange sites, and tunable Brønsted/Lewis acidity. ZSM-5 has intersecting ten-membered-ring channels and can host exchanged Cu, Co, Fe, or Ni species while imposing shape and diffusion constraints. Alkali-modified Cu-Na-ZSM-5 was shown to favor partial oxidation of benzyl alcohol relative to deep oxidation, demonstrating that the neighborhood of Cu and support basicity can alter selectivity [13, 14]. Zeolite-Y has larger supercages and has been widely used to encapsulate Cu, Ni, and Co complexes, producing recyclable heterogeneous oxidation catalysts [15, 16].

ZSM-22 is a one-dimensional ten-membered-ring zeolite with narrow channels. Its topology can be advantageous when shape selectivity, controlled residence time, or isolated exchanged metal ions are desired, but one-dimensional diffusion also increases the risk of pore blocking. Compared with ZSM-5, direct literature on non-noble-metal/ZSM-22 for selective alcohol-to-carbonyl oxidation is limited. Thus, ZSM-22 should presently be treated as an emerging support rather than as an established benchmark. Hierarchical ZSM-22, external-surface metal deposition, and low metal loading are logical strategies to overcome diffusion limitations.

3.3 SBA-15

SBA-15 is an ordered mesoporous silica possessing two-dimensional hexagonally arranged channels, relatively large pore diameters, thick silica walls, and high hydrothermal stability [40, 41]. These features make it particularly suitable for immobilizing non-noble transition-metal nanoparticles, oxides, and isolated metal species while retaining access to

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bulky alcohol substrates. Cu-, Mn-, Co-, Fe-, Ni-, and V-containing SBA-15 materials can be prepared by impregnation, deposition-precipitation, grafting, ion-assisted anchoring, or direct synthesis. Compared with microporous zeolites, the wider mesopores of SBA-15 reduce diffusion limitations and facilitate product desorption, which can help suppress secondary oxidation of aldehydes. At the same time, the silanol-rich surface can stabilize highly dispersed metal species and may be modified with amino, thiol, or other anchoring groups to reduce sintering and leaching. The principal structure-activity parameters are metal particle size, location inside versus outside the mesopores, degree of pore blockage, metal-support interaction, and preservation of the ordered channel system. For selective alcohol oxidation, SBA-15 is therefore an important bridge between high-surface-area mesoporous supports and practical heterogeneous catalyst design.

3.4 MCM-41

MCM-41 contains an ordered hexagonal array of mesopores, normally with high surface area and abundant silanol groups [17, 18]. Its larger channels reduce diffusion resistance for bulky aromatic or biomass-derived alcohols and allow metal oxides to be dispersed as small domains. MnOx/MCM-41 demonstrates the importance of precursor chemistry: manganese precursor and calcination temperature determine Mn oxidation state and reducibility, with Mn4+/Mn3+-rich surface oxo species displaying higher intrinsic activity than Mn2+-rich materials [19]. V-MCM-41 also illustrates the value of framework incorporation; well-dispersed V4+/V5+ species gave substantial benzyl alcohol conversion with high benzaldehyde selectivity [20]. Cu-containing functionalized MCM-41 systems further show that pore-wall chemistry can immobilize active Cu species while retaining solvent-free oxidation capability [21, 22].

IV. MONOMETALLIC NON-NOBLE TRANSITION-METAL CATALYSTS

4.1 Copper

Copper is among the most versatile non-noble metals for alcohol oxidation because Cu(I)/Cu(II) cycling can couple alcohol dehydrogenation with oxygen or peroxide activation. On porous supports, isolated Cu ions, CuOx clusters, and CuO nanoparticles can coexist. High dispersion generally favors selective carbonyl formation, whereas large CuO domains may promote unselective peroxide decomposition. In Cu-zeolites, ion-exchange position and neighboring alkali ions modify electron density and adsorption. In mesoporous silica, anchoring groups or surface silanols suppress aggregation. The practical design target is therefore not simply high Cu loading but a high density of accessible, redox-active Cu sites with limited Cu leaching.

4.2 Manganese

Manganese oxides offer $Mn^{2+}/Mn^{3+}/Mn^{4+}$ redox flexibility, mobile lattice oxygen, and defect chemistry. Supported MnOx is especially effective when high-valent, reducible surface oxo species are stabilized. MnOx/MCM-41 and K-Mn/gamma-Al_2O_3 establish two complementary strategies: mesoporous dispersion and promoter-induced phase control [12, 19]. Recent morphology studies on alpha-MnO_2 also reinforce the correlation between oxygen vacancies, reducibility, and benzyl alcohol oxidation rate [23]. Excessive oxygen mobility, however, can lower aldehyde selectivity, making residence time and oxygen chemical potential important process variables.

4.3 Cobalt, Iron, Nickel, and Vanadium

Co_3O_4 contains both Co^{2+} and Co^{3+} and can activate oxygen through surface redox cycles. Supported Co_3O_4 performance depends on crystallite size, support functionality, and the abundance of Co^{3+}-O motifs [24]. Iron is inexpensive and environmentally attractive; Fe-based sites can activate H_2O_2 through Fenton-like chemistry, but uncontrolled radical pathways may reduce selectivity. Confinement of iron complexes in MCM-41 has been shown to stabilize the active Fe-O-Fe environment during benzyl alcohol oxidation [25]. Nickel is usually less active than Cu or Mn for mild aerobic oxidation but can contribute to bimetallic redox ensembles. Vanadium, particularly isolated tetrahedral or oligomeric V species, is effective for peroxide oxidation; V-MCM-41 provides a direct example of how framework dispersion and valence distribution translate to selective oxidation [20].

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V. BIMETALLIC CATALYSTS AND SYNERGISTIC INTERFACES

Bimetallic design can outperform a monometallic catalyst when the second metal changes electronic structure, oxygen-vacancy formation, redox potential, adsorption geometry, or dispersion. Synergy should not be inferred merely from the presence of two metals; it should be demonstrated against both monometallic controls at comparable total loading. Cu-Ni nanoparticles supported on activated carbon showed improved benzyl alcohol oxidation at an optimum composition, illustrating a composition-dependent bimetallic effect [26]. Cu-Mn systems are particularly promising because Cu facilitates electron transfer while Mn supplies redox-active lattice oxygen. $CuMn_2O_4$ spinel studies directly correlate higher surface oxygen-vacancy concentration with improved aerobic benzyl alcohol oxidation and high benzaldehyde selectivity [27]. Cu-Mn/activated carbon likewise shows a strong dependence on metal ratio [28]. Other rational combinations include Cu-Co, Cu-Fe, Fe-Mn, and Ni-Co. Cu-Co can combine rapid Cu redox cycling with oxygen activation on cobalt oxide; Cu-Fe may couple Cu-mediated alcohol activation with Fe-mediated peroxide activation; and Fe-Mn can broaden the redox window and oxygen mobility. For porous supports, the key structural question is whether both metals occupy the same nanoparticle, form mixed oxides, sit as neighboring isolated ions, or segregate into separate domains. XPS shifts alone are insufficient proof. STEM-EDS mapping, X-ray absorption spectroscopy, and, where possible, operando measurements are required to establish the active bimetallic interface.

Technique	Primary information
XRD/SAXRD	Crystalline phases; zeolite crystallinity; MCM-41 ordering; crystallite size
N2 physisorption (BET/BJH or NLDFT)	Surface area, pore volume, pore-size distribution
SEM/TEM/HRTEM/STEM-EDS	Morphology, particle size, lattice fringes, elemental co-location
XPS	Surface composition, Cu/Co/Fe/Mn/V oxidation states, O 1s defect species
UV-Vis DRS/Raman	Coordination of isolated ions vs oxide clusters; metal-oxygen vibrations
H2-TPR	Reducibility and metal-support interaction
O2-TPD/O2 chemisorption	Adsorbed oxygen strength and oxygen mobility
NH3-TPD + pyridine-FTIR	Total acidity and Brønsted/Lewis acid distribution
ICP-OES/ICP-MS	Bulk loading and leached metal in filtrate
In situ/operando XAS, DRIFTS, Raman	Dynamic oxidation state, coordination and adsorbates under reaction

VI. ADVANCED CHARACTERIZATION AND TECHNIQUE

A credible structure-activity relationship requires characterization before reaction, after activation and after recycling. No single technique can establish the active phase. The following toolbox is recommended for porous-supported non-noble-metal oxidation catalysts [29-35].

Structure-activity question

For SBA-15 and MCM-41, low-angle XRD should verify preservation of the ordered mesostructure, while wide-angle XRD checks for crystalline metal-oxide phases. For zeolites, preservation of the characteristic framework pattern is essential. BET surface area should never be interpreted alone: decreases in area and pore volume can indicate successful pore filling, but severe losses suggest blockage. XPS must be combined with bulk ICP data because XPS is surface-sensitive. H2-TPR is especially valuable for Cu, Mn, Co and Fe oxides because reduction temperature reflects dispersion and metal-support interaction. Acid characterization is mandatory for ZSM-5 and ZSM-22, since strong acidity can promote dehydration or condensation pathways unrelated to the desired oxidation.

Post-reaction analysis is equally important. Hot-filtration tests, ICP analysis of the liquid phase, reuse experiments and post-use XRD/TEM/XPS distinguish genuine heterogeneous turnover from leached homogeneous species. A catalyst that maintains conversion but loses selectivity may have undergone subtle oxidation-state or acidity changes even when XRD remains unchanged.

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VII. STRUCTURE-ACTIVITY RELATIONSHIPS

Four descriptors recur across successful systems. First, metal dispersion determines the fraction of accessible redox sites. Second, oxidation-state flexibility controls the ease of closing the catalytic redox cycle. Third, oxygen vacancies and labile surface oxygen facilitate O2 activation and lattice-oxygen replenishment, particularly for Mn- and mixed Cu-Mn oxides [27]. Fourth, pore architecture controls transport and local concentration. SBA-15 and MCM-41 favour accessibility and diffusion of bulky substrates; zeolites can provide shape selectivity and isolated exchanged ions; alumina offers robust anchoring and process stability.

These descriptors are coupled. Increasing metal loading may raise the number of sites but simultaneously decrease dispersion and pore volume. Strong metal-support interaction can stabilize small particles but shift reduction to temperatures too high for mild oxidation. Strong zeolite acidity can improve adsorption but also retain polar aldehydes, increasing secondary reactions. Therefore, optimum catalysts often lie at intermediate loading, intermediate redox strength, and balanced acidity rather than at the maximum value of any single property.

Bimetallic catalysts add another level: the distance between dissimilar metal centers. True cooperative sites require nanoscale proximity. If Cu and Mn are separated into large CuO and MnO2 particles, their behavior may simply be additive. Mixed oxides, spinels or adjacent exchanged ions can instead create new oxygen-vacancy energies and electron-transfer pathways. Demonstrating this requires composition series, monometallic controls and spectroscopic evidence.

VIII. OXIDANTS, SOLVENTS AND SUSTAINABLE PROCESS DESIGN

Molecular oxygen and air generate water as the ideal coproduct and are preferred for large-scale sustainability, but safe gas-liquid mass transfer and avoidance of flammable mixtures are critical. H2O2 is attractive because it is easy to handle in dilute aqueous form and also yields water, although nonproductive decomposition can lower oxidant efficiency. TBHP often gives high laboratory conversion but produces tert-butanol and is less attractive for waste-minimized manufacture. Accordingly, catalyst comparisons should report oxidant utilization, not only substrate conversion.

Solvent-free oxidation reduces solvent intensity and can increase volumetric productivity, but viscosity and heat removal may become limiting. Water, ethanol, ethyl acetate and other lower-impact solvents are preferable where compatible with catalyst stability. Acetonitrile and toluene are common research solvents but should be justified. Process metrics should include carbonyl yield, selectivity, turnover frequency where reliable, space-time yield, E-factor or process mass intensity, metal leaching, catalyst lifetime and energy demand [36-39].

Continuous gas-phase oxidation over supported Cu, Mn or mixed oxides is attractive for volatile alcohols because catalyst separation is inherent and oxygen can be supplied continuously. For liquid substrates, trickle-bed or continuous-flow peroxide processes may provide improved heat and mass transfer. Translation from batch screening to process development requires shaped catalysts, pressure-drop evaluation, long-duration stability, regeneration protocols and testing with realistic feed impurities.

IX. REPRESENTATIVE MONOMETALLIC AND BIMETALLIC POROUS-SUPPORTED CATALYSTS

Table 1 summarizes representative monometallic systems for which the metal identity and porous support are explicitly defined. Broad labels such as “non-noble metal/SBA-15” are avoided because catalyst performance depends on the specific metal phase, loading, preparation route and pore environment.

Table 1. Representative monometallic non-noble transition-metal catalysts on porous supports for selective alcohol oxidation.

Catalyst / porous support	Oxidant / conditions	Conversion / selectivity	Characterization-linked design lesson	Ref.
Cu/SBA-15	30% H2O2; water; 353 K; 6 h	47.6% conversion; 84.8% benzaldehyde	XRD/FTIR showed preserved SBA-15 mesostructure and Cu-O-Si	[51]

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		selectivity	interaction; reusable for four runs	
MnOx/SBA-15	TBHP; CH3CN; 90 °C; 8 h	70% conversion; 100% benzaldehyde selectivity	ICP, XRD, Raman, UV-Vis and N2 physisorption linked highly dispersed Mn2+/Mn3+ redox pairs to activity; negligible leaching	[52]
MnOx/MCM-41	H2O2	Selective benzyl alcohol oxidation	Precursor/calcination controlled Mn oxidation state, dispersion and reducibility in ordered mesopores	[19]
V-MCM-41	Oxidative conditions	High benzaldehyde selectivity reported	Ordered MCM-41 stabilized dispersed V4+/V5+ species; framework/oxo speciation controlled activity	[20]
K-Mn/gamma-Al2O3	O2	Aerobic benzyl alcohol oxidation	K promotion modified supported MnOx structure and reducibility, illustrating promoter-support-redox coupling	[12]
Cu-Na-ZSM-5	O2/air	Partial oxidation of benzyl alcohol	Alkaline environment near Cu altered adsorption/basicity and suppressed deep oxidation	[13,14]

Bimetallic systems should be evaluated against both corresponding monometallic catalysts at comparable total loading. The most persuasive studies connect improved performance to nanoscale metal proximity, altered reducibility or oxygen-vacancy chemistry rather than merely reporting the presence of two metals.

Table 2. Representative bimetallic non-noble transition-metal catalysts relevant to porous-supported selective alcohol oxidation.

Bimetallic catalyst / porous support	Oxidant/conditions	Conversion/selectivity	Evidence for bimetallic advantage	Ref.
Ni-Fe/SBA-15 (NFS-15)	TBHP; optimized liquid-phase conditions	98% conversion; 99% benzaldehyde selectivity; reusable up to 7 cycles	XRD, BET and TEM supported high dispersion; composition optimization demonstrated a strong Ni-Fe/SBA-15 performance window	[53]
Ni-Co/SBA-15	Air; atmospheric pressure	Selective oxidation of benzyl alcohols	Mesoporous silica-supported Ni-Co composite oxide; catalytic performance strongly depended on synergistic interaction between Ni and Co ions	[54]
Cu-Ni/activated porous carbon*	H2O2	Benzyl alcohol oxidation	Composition-dependent activity demonstrated Cu-Ni synergy; useful comparison for transferring bimetallic design principles to ordered porous supports	[26]
Cu-Mn/activated porous carbon*	Oxidative conditions	Benzyl alcohol oxidation	Metal ratio strongly affected catalytic performance, consistent with coupled Cu-Mn redox chemistry	[28]

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X. RESEARCH GAPS AND FUTURE DIRECTIONS

Several gaps prevent straightforward ranking of non-noble porous catalysts. Reaction conditions vary widely, and many reports omit carbon balance, intrinsic rate, oxidant efficiency, or leaching. Future studies should use standardized metrics and include blank tests, mass-transfer checks, and monometallic controls. For bimetallic materials, a full composition series is more informative than a single nominal ratio.

Operando characterization is a priority because Cu, Mn, Co, and Fe can restructure under oxidizing conditions. Combining XAS or ambient-pressure XPS with DRIFTS and isotopic oxygen experiments can distinguish lattice-oxygen, adsorbed-oxygen, and peroxide pathways. Computational screening should focus on experimentally measurable descriptors such as oxygen-vacancy formation energy, alcohol adsorption energy and alpha-C-H activation barrier.

Support engineering also remains underexploited. Hierarchical ZSM-5 and ZSM-22 can combine micropore selectivity with mesopore transport. Dealumination or controlled alkali exchange can tune acidity independently of metal loading. SBA-15 and MCM-41 can be functionalized to strengthen metal anchoring, while alumina surface hydroxyl populations can be controlled by pretreatment. Particularly promising are Cu-Mn, Cu-Co, Cu-Fe and Fe-Mn pairs dispersed as sub-nanometer clusters or neighbouring ions on these supports. ZSM-22 warrants systematic investigation with such earth-abundant bimetallic pairs, as its one-dimensional topology may confer distinct selectivity if diffusion limitations are deliberately managed.

Finally, sustainability must be demonstrated at the process level. A catalyst prepared by a hazardous reducing agent or energy-intensive multistep route may offset the benefit of using air as oxidant. Water-based impregnation, deposition-precipitation, ion exchange, and low-temperature activation should be prioritized. Catalyst lifetime over tens to hundreds of hours, regeneration, metal recovery, and support recyclability should become standard evaluation criteria.

X1. CONCLUSION

Porous-supported non-noble transition metals provide a credible platform for selective alcohol oxidation when metal chemistry and pore architecture are designed together. Cu, Mn, Co, Fe, Ni, and V can generate active redox sites without relying on noble metals, while gamma-Al2O3, zeolites, ZSM-5, ZSM-22, SBA-15, and MCM-41 control dispersion, acidity, confinement, and molecular transport. The strongest evidence currently links high dispersion, accessible mixed valence, controlled oxygen vacancies and balanced acid-base properties with high carbonyl selectivity. SBA-15 and MCM-41 are advantageous for diffusion and dispersion, ZSM-5 and other zeolites for confinement and ion-exchange control, alumina for robust anchoring, and ZSM-22 represents a comparatively unexplored opportunity. Bimetallic systems are most compelling when spectroscopy proves a new interfacial redox environment rather than simple coexistence of two phases. Future progress will depend on operando characterization, rigorous heterogeneity tests, standardized catalytic metrics, and process-relevant stability. These principles can guide the development of recyclable, earth-abundant catalysts for O2-, air-, or H2O2-mediated oxidation under solvent-minimized and continuous conditions.

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