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Mesoporous versus Microporous Supports for Noble Metal Catalysis: A Critical Comparative Review .

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Abstract : *Noble-metal catalysts (Pt, Pd, Ru, and Rh) are efficient activators of H_2, O_2, CO, NO, carbonyl compounds, and unsaturated organic molecules and, consequently, are significant in heterogeneous catalysis. Catalyst structures are expensive and susceptible to sintering; hence, the metal surface needs to be maximized while maintaining activity and stability. Porous supports modulate noble-metal dispersion, particle size, metal-support interaction, and reactant transport. Two alternative ways of active-site engineering are the order of mesoporous materials such as SBA-15 and MCM-41 and microporous zeolites such as ZSM-5, ZSM-22, Beta, and Y. Mesoporous materials are suitable for interactions with complicated organic substrates because of open molecular transport and high surface area and large pore volume. Microporous zeolites can accommodate isolated atoms, clusters, and nanoparticles due to their molecular-scale confinement, shape selectivity, ion-exchange capacity, and variable acidity. But their small channels can restrict diffusion greatly and contribute to pore blockage. This paper presents an objective examination of mesoporous and microporous supports for Pt-, Pd-, Ru-, and Rh-based catalysts with emphasis on pore architecture, metal dispersion, metal-support interaction, acidity, reducibility, molecular transport, and catalytic activity. Detailed discussion on the importance of XRD/SAXRD, N_2 physisorption, TEM/STEM, XPS, H_2-TPR, NH_3-TPD, and chemisorption for the establishment of structure-activity correlations. Oxidation, hydrogenation, environmental catalysis, and bifunctional reactions are stressed. The review shows that mesopores provide access while micropores cause confinement and molecular recognition. Hierarchical micro-mesoporous materials may offer the advantages of both types of porosity.*

Key Words: Noble metals; heterogeneous catalysis; mesoporous materials; microporous materials; metal–support interaction.

1. INTRODUCTION

Supported noble-metal catalysts are indispensable in modern heterogeneous catalysis. Platinum, palladium, ruthenium and rhodium possess favourable electronic structures for adsorption and activation of hydrogen, oxygen, carbon monoxide, nitrogen oxides, carbonyl compounds and unsaturated hydrocarbons. Consequently, these metals are used extensively in hydrogenation, selective oxidation, automotive emission control, reforming, fine-chemical synthesis and biomass upgrading. Their major limitation is economic: noble metals are scarce and expensive. In addition, small metal nanoparticles tend to migrate, agglomerate or undergo chemical transformation during thermal and catalytic operation. Efficient catalysts must therefore expose the maximum number of catalytically useful metal atoms while stabilizing them against deactivation.

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The concept of using a high-surface-area support to disperse a noble metal is well established. Nevertheless, the support should no longer be considered a chemically inert carrier. Its surface composition, pore architecture, acidity, redox properties and interaction with the metal can substantially influence the identity of the active site and the observed reaction pathway. In porous catalysts, the geometric relationship between the metal particle, support pore and reacting molecule becomes particularly important.According to the conventional IUPAC classification, micropores have widths of approximately ≤2 nm, whereas mesopores extend from about 2 to 50 nm. The discovery of ordered M41S materials such as MCM-41 and, subsequently, SBA-15 opened new possibilities for tailoring mesopore dimensions, connectivity, and surface chemistry [1–3]. In parallel, zeolites such as ZSM-5, ZSM-22, Beta, Y, and mordenite remain among the most technologically important microporous catalysts because of their crystallinity, shape selectivity, acidity, and ion-exchange capacity [4–6].

Pore architecture influences more than surface area. It determines whether noble-metal particles form within pores or on external surfaces, how readily reactants reach the active sites, whether reaction intermediates are stabilized by confinement, and how effectively the support suppresses metal sintering. Mesoporous silicas commonly provide wide and accessible channels capable of accommodating metal nanoparticles and relatively bulky molecules. Zeolitic micropores, in contrast, generate molecular-scale catalytic environments capable of stabilizing ions, single atoms, clusters and encapsulated nanoparticles while discriminating between reactants and products according to size and shape [7–9].

A simple comparison based only on BET surface area is therefore inadequate. A support with a very high surface area may contain metal species that are poorly accessible, while a material of lower total surface area may display greater catalytic productivity because a larger fraction of its metal is exposed to the reacting molecules. This distinction gives rise to an important catalytic concept: total metal dispersion and catalytically accessible metal dispersion are not necessarily equivalent. The purpose of the present review is to critically compare mesoporous and microporous supports for noble-metal catalysis. Particular emphasis is placed on SBA-15 and MCM-41 as representative mesoporous materials and ZSM-5, ZSM-22, Beta and Y as representative zeolitic supports. The discussion centres on Pt, Pd, Ru and Rh catalysts and examines how pore architecture modifies metal dispersion, confinement, acidity, reducibility, transport phenomena, catalytic activity, selectivity and stability.

II. PORE ARCHITECTURE AS A CATALYST DESIGN PARAMETER

The catalytic significance of porosity depends on more than average pore diameter. Pore connectivity, channel dimensionality, pore-mouth dimensions, crystal size, surface hydroxyl density and the presence of cages or intersections can all influence catalytic behaviour.

MCM-41 consists of a regular hexagonal arrangement of essentially one-dimensional cylindrical mesopores and typically exhibits a very high surface area [1,2]. SBA-15 also possesses an ordered hexagonal architecture but generally contains larger mesopores and thicker silica walls, which improve hydrothermal and thermal stability [3]. These mesostructures can act as nanoscale reactors in which metal nanoparticles are deposited or generated. Microporous zeolites consist of crystalline three-dimensional aluminosilicate or silicate frameworks constructed from interconnected TO_4 tetrahedra. Their channel dimensions are comparable to molecular dimensions. ZSM-5 possesses an intersecting medium-pore network, whereas ZSM-22 is characterized by essentially one-dimensional channels. Zeolite Beta and Y contain larger pore openings and cavities and therefore provide comparatively greater accessibility than medium-pore zeolites.The major differences are summarized in Table 1.

Table 1. General comparison of mesoporous and microporous noble-metal catalyst supports

Property	Mesoporous supports	Microporous supports
Representative materials	SBA-15, MCM-41, KIT-6	ZSM-5, ZSM-22, Beta, Y
Typical pore size	2–50 nm	≤2 nm
Noble-metal accommodation	Nanoparticles readily	Ions, atoms, clusters; larger particles mainly in

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Property	Mesoporous supports	Microporous supports
	accommodated	cages/external surface
Molecular diffusion	Relatively rapid	Often restricted
Bulky-substrate accessibility	High	Low to moderate
Confinement strength	Moderate	Strong
Shape selectivity	Limited	High
Intrinsic acidity	Low for pure silica	Tunable, often strong
Metal sintering resistance	Good when confined	Potentially excellent
Pore blockage sensitivity	Moderate	High
Metal–acid bifunctionality	Requires modification	Readily achievable
Principal advantage	Accessibility	Molecular confinement
Principal limitation	Weaker molecular discrimination	Diffusion resistance

This comparison immediately illustrates why neither type of support can be regarded as universally superior. Mesoporous materials are advantageous when fast diffusion and access of large molecules are required, whereas microporous supports are particularly attractive when molecular discrimination, strong confinement or bifunctional metal–acid catalysis is desired.

III. INFLUENCE OF MESOPOROSITY ON NOBLE-METAL DISPERSION AND CATALYSIS

Mesoporous supports such as MCM-41 and SBA-15 provide an extensive internal surface for the deposition of noble metals. Metal precursors may be introduced by incipient-wetness impregnation, wet impregnation, deposition–precipitation, grafting, ion-assisted adsorption or direct synthesis. Subsequent reduction or calcination produces metallic or oxidic species whose size and location are influenced by the pore dimensions and surface chemistry.

If nanoparticles are formed inside the pores, channel walls can restrict their growth and mobility. This physical confinement is weaker than true zeolitic encapsulation but can nevertheless suppress extensive agglomeration. An appropriate relation between nanoparticle diameter and pore diameter is therefore important. Very wide pores provide excellent accessibility but weak physical restriction, whereas excessively narrow pores may be partially blocked by the deposited metal.

SBA-15 is especially attractive because of its comparatively large and ordered channels and thick silica walls. Its silanol-rich surface can be functionalized with amino, thiol or other groups to anchor noble-metal precursors. Such functionalization is frequently used to improve Pd or Pt dispersion and reduce leaching in liquid-phase catalysis [10]. MCM-41 provides similarly high internal surface area but generally possesses thinner walls and may be less stable under harsh hydrothermal conditions.The importance of mesopore architecture was demonstrated for Pd-catalysed aerobic alcohol oxidation, where different mesoporous silica structures produced significant changes in catalytic rate. Interconnected mesoporous frameworks improved both metal dispersion and mass transport compared with conventional silica [11]. This example highlights a general feature of mesoporous catalysis: pore connectivity can be as important as pore diameter.Mesoporous supports are particularly suitable for selective oxidation of alcohols, hydrogenation of aromatic carbonyl compounds, C–C coupling and biomass-related reactions because relatively large organic molecules can enter their channels. The absence of severe configurational diffusion limitations ensures that a considerable fraction of the internal metal surface can participate in catalysis.

The principal limitation of pure mesoporous silica is its relatively inert framework. Metal–support interactions may be weaker than those available on reducible oxides or acidic zeolites. Consequently, metal nanoparticles can migrate during high-temperature operation unless they are properly anchored. Incorporation of Al, Ti, Zr, Ce or other heteroatoms into the mesostructure is an important strategy for tuning acidity, redox behaviour and metal stabilization

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IV. MICROPOROUS ZEOLITES: CONFINEMENT, SHAPE SELECTIVITY AND BIFUNCTIONALITY

Zeolite-supported noble metals represent a different catalytic design concept. Their micropores are comparable in dimension to reactants and reaction intermediates, producing molecular-scale confinement.Noble metals may be introduced through ion exchange, impregnation, one-pot encapsulation or post-synthetic incorporation. Depending on preparation and framework structure, metal species may exist as exchanged cations, single atoms, subnanometric clusters, nanoparticles in cages or particles on the external crystal surface. The exact metal location is crucial because it determines accessibility, stability and catalytic selectivity.

Zeolite confinement can strongly suppress nanoparticle migration and coalescence [7–9]. Encapsulation is particularly effective because the surrounding crystalline framework acts as a physical barrier against sintering. Metal@zeolite catalysts have therefore attracted considerable interest for reactions performed under severe thermal conditions. Encapsulation can also improve resistance to metal leaching in liquid-phase systems.

Another distinctive feature is shape-selective catalysis. Three forms may be distinguished. In reactant shape selectivity, only molecules sufficiently small to enter the pore can reach internal active sites. In product shape selectivity, product diffusion is governed by molecular dimensions. In transition-state selectivity, the pore environment preferentially stabilizes reaction pathways whose transition states fit within the available cavity.

Zeolites also provide tunable Brønsted and Lewis acidity. In aluminosilicate zeolites, the substitution of Si^{4+} by Al^{3+} creates framework negative charge that may be balanced by protons or metal cations. Noble-metal/zeolite catalysts can therefore be bifunctional: the metal can perform hydrogenation, dehydrogenation or redox chemistry while acid sites catalyse cracking, dehydration or isomerization. Pt/zeolite catalysts used in hydroisomerization are a classical example of such bifunctionality.

The major disadvantage of microporosity is restricted molecular transport. Pérez-Ramírez and co-workers emphasized that intracrystalline diffusion limitations can prevent full utilization of zeolite active volume [12]. This becomes particularly important for bulky substrates, strongly adsorbed intermediates or rapidly reacting systems. Microporous catalysts may therefore contain highly dispersed metal species that make only a limited contribution to the measured reaction rate because access to them is kinetically restricted.

V. MESOPOROUS VERSUS MICROPOROUS CONTROL OF METAL DISPERSION

Noble-metal dispersion is often used as an indicator of catalyst quality because smaller particles expose a higher fraction of metal atoms. However, the catalytic significance of dispersion depends strongly on reaction mechanism.Mesoporous materials generally control dispersion by distributing metal precursors over a large internal area and spatially restricting particle growth. The resulting particles are commonly several nanometres in size and remain accessible to relatively large molecules.

Microporous zeolites may stabilize much smaller species through electrostatic interactions, ion exchange and steric confinement. Single atoms and subnanometric clusters can be stabilized at framework-associated sites. Nevertheless, a metal nanoparticle larger than the pore aperture cannot freely move through the zeolite channel. Therefore, the final catalyst may contain a complex distribution of internal ionic species, encapsulated clusters and external nanoparticles.The correlation between particle size and catalytic performance is also reaction dependent. Structure-sensitive reactions require particular surface ensembles, and excessively small clusters may display different adsorption energies and product selectivities from conventional nanoparticles. Consequently, maximizing dispersion alone is not a sufficient design criterion.

A more useful parameter is accessible, stable and catalytically appropriate dispersion. This concept accounts simultaneously for the number of exposed metal atoms, molecular accessibility, electronic state, and resistance to deactivation

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VI. METAL–SUPPORT INTERACTION AND ELECTRONIC EFFECTS

The metal–support interaction influences precursor deposition, metal oxidation state, particle morphology, reducibility, and adsorption properties. For silica-rich SBA-15 and MCM-41, interaction with noble metals commonly involves surface silanol groups. Although these interactions can stabilize small particles, they are often weaker than interactions provided by reducible oxides or zeolitic exchange sites.

Modification of mesoporous silica with heteroatoms or functional groups can therefore produce major changes in noble-metal behaviour. Amino-functionalized SBA-15, for example, can strongly coordinate Pd precursors, facilitating uniform metal distribution. Incorporation of ceria or titania introduces redox-active interfaces capable of influencing oxygen activation and electron transfer. Zeolites provide chemically more heterogeneous environments. Framework Al atoms, ion-exchange positions, Brønsted acid sites, silanol nests and defects can act as anchoring sites. Noble-metal species confined near framework Al may experience substantial electrostatic and electronic stabilization.

Strong interaction is not always beneficial. If metal species become too strongly bound, reduction may require higher temperatures and the concentration of accessible metallic sites may decrease. Conversely, excessively weak interaction facilitates reduction but promotes particle migration and sintering. Optimum catalysts require an intermediate regime in which the metal is sufficiently stabilized but remains chemically accessible. This balance can be represented conceptually as:

Weak MSI → high mobility and sintering. Excessively strong MSI → difficult reduction or restricted reactivity. Optimized MSI → stable, accessible, and electronically favourable active sites

VII. DIFFUSION, ACCESSIBILITY AND CONFINEMENT EFFECTS

Mass transport provides perhaps the most fundamental distinction between mesoporous and microporous supports. In mesoporous materials, channel widths substantially exceed the dimensions of many organic molecules. Consequently, benzyl alcohol, substituted aromatic alcohols, ketones and many biomass-derived substrates can diffuse through the support with comparatively low resistance. Wider channels also facilitate removal of products and reduce residence time of strongly adsorbed intermediates that could lead to overreaction or coke formation. Microporous zeolites operate close to the molecular dimensions of the reacting species. Such confinement can be beneficial because it increases interaction between adsorbates and pore walls and can stabilize specific configurations. However, it can also result in strong diffusional resistance. The catalytic rate measured for a porous material therefore contains both intrinsic kinetic and transport contributions. A microporous catalyst may possess exceptionally active internal sites but display a modest overall conversion because transport to these sites is rate-limiting. This leads to a crucial distinction: High total surface area ≠ high accessible surface area and High metal dispersion ≠ high accessible metal dispersion.For bulky molecules, a moderately dispersed metal in wide mesopores may be more catalytically productive than atomically dispersed metal located in inaccessible micropores.

VIII. COMPARATIVE BEHAVIOUR OF PT, PD, RU AND RH

8.1 Platinum

Pt is widely employed in hydrogenation, reforming, oxidation and environmental catalysis. Pt nanoparticles supported within SBA-15 or MCM-41 benefit from high surface area and large substrate-accessible pores. Such architectures are suitable for organic transformations involving bulky substrates.Pt/zeolite catalysts exploit different phenomena. The zeolite may stabilize small Pt species and simultaneously provide acid sites. This metal–acid cooperation is particularly important in hydroisomerization and hydrocracking. The metal activates hydrogen and performs hydrogenation–dehydrogenation steps, while zeolitic acid sites catalyse skeletal rearrangement or cracking. Encapsulated Pt species can exhibit excellent thermal stability, but catalytic performance may become transport-limited for larger reactants. Therefore, Pt/mesoporous materials favour accessibility, whereas Pt/zeolite systems often favour bifunctionality and stability.

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8.2 Palladium

Pd is among the most extensively studied noble metals in selective oxidation, hydrogenation, coupling chemistry and exhaust treatment. Mesoporous silica can disperse Pd nanoparticles over a high internal area while allowing direct contact with bulky organic substrates. SBA-15-supported Pd materials have therefore been widely investigated in C–C coupling and oxidation reactions [10,11].Pd in zeolites may occur as Pd^{2+} ions, PdO species, metallic clusters or encapsulated nanoparticles. Zeolite confinement can suppress sintering and create shape-selective behaviour. For small-molecule reactions, especially those relevant to emission control, this strong stabilization can be highly advantageous.

The comparison may therefore be simplified as : Pd/mesoporous silica: accessibility and large-molecule conversion,Pd/zeolite: confinement, stability and molecular discrimination

8.3 Ruthenium

Ru is an efficient catalyst for hydrogenation, hydrogenolysis and several energy-related reactions. Mesoporous MCM-41 and SBA-15 can provide high Ru dispersion together with rapid diffusion of ketones, aromatic compounds and other reactants.When Ru is supported on acidic microporous zeolites, the catalytic behaviour reflects not only metal dispersion but also the combined effects of pore restrictions and acidity. Strong metal–support interaction may stabilize small Ru species, but narrow channels may limit substrate access or alter the sequence of hydrogenation reactions.For reactions in which complete hydrogenation of an aromatic substrate requires repeated access to Ru sites, mesoporous supports can be especially favourable. Conversely, zeolitic confinement can be useful when selective partial transformation or high thermal stability is required.

8.4 Rhodium

Rh is highly active in hydrogenation, hydroformylation, and NO conversion. Because of its high cost, efficient utilization of Rh atoms is particularly important. Mesoporous materials provide high accessibility to Rh nanoparticles, while zeolite frameworks are attractive for stabilizing small clusters and isolated species. The strong confinement possible within zeolitic cages can inhibit Rh migration and maintain high dispersion during thermal treatment. Future developments are likely to focus increasingly on isolated Rh atoms and subnanometric clusters because these architectures maximize noble-metal atom efficiency.

IX. CHARACTERIZATION: ESTABLISHING STRUCTURE–ACTIVITY RELATIONSHIPS

A meaningful comparison of mesoporous and microporous catalysts requires complementary characterization. No single technique can establish metal location, particle size, pore accessibility, and electronic state simultaneously.

9.1 X-ray diffraction

Wide-angle XRD provides information on support crystallinity and crystalline metal phases. Zeolites exhibit characteristic framework diffraction patterns, whereas larger noble-metal crystallites may produce detectable reflections.

The absence of a noble-metal diffraction peak should not automatically be interpreted as absence of the metal. It may indicate low loading, very small particle size, amorphous species, or high dispersion. For ordered mesoporous materials, small-angle XRD or SAXS is particularly useful. SBA-15 commonly displays characteristic reflections associated with its hexagonal arrangement. Retention of these peaks after metal incorporation indicates preservation of mesoscopic ordering.

9.2 N_2 physisorption

BET surface area, total pore volume and pore-size distribution are essential for evaluating structural changes after metal loading. A decrease in surface area and pore volume may indicate occupation of the internal pores, although substantial loss can also indicate pore blockage.For microporous zeolites, micropore volume is especially informative. Comparison of textural data before and after metal loading can help determine whether deposited species obstruct internal channels.

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9.3 TEM and STEM

Transmission electron microscopy is one of the most direct methods for measuring nanoparticle size and distribution. High-angle annular dark-field STEM is highly useful for noble-metal catalysts because heavy metals provide strong contrast relative to silica or aluminosilicate supports.Electron tomography and advanced STEM techniques can provide further information about whether particles are inside pores or on external surfaces. Nevertheless, distinguishing deep encapsulation from projection effects remains challenging.

9.4 X-ray photoelectron spectroscopy

XPS identifies surface oxidation states and electronic changes. Shifts in Pt, Pd, Ru or Rh binding energies may provide evidence of electron transfer between metal and support.However, XPS probes only a limited near-surface depth. A low measured metal concentration may therefore result from successful encapsulation rather than low total loading. XPS results should consequently be combined with bulk elemental analysis.

9.5 H_2-TPR

H_2-temperature-programmed reduction provides information about the reducibility of supported metal species and, indirectly, their interaction with the support. Lower reduction temperatures often indicate easily reducible surface species, whereas shifts to higher temperature can reflect stronger interaction or more stable oxidic species.
Reduction temperature should not, however, be used alone to predict catalytic activity. Easily reducible particles may also be poorly dispersed, whereas strongly stabilized species may become highly active after appropriate activation.

9.6 Acidity measurements

NH_3-TPD is useful for assessing total acidity and acid-strength distribution, particularly in zeolite catalysts. Pyridine-adsorbed infrared spectroscopy can distinguish Brønsted and Lewis acid sites.These measurements are essential for bifunctional noble-metal/zeolite systems because differences in product distribution may originate from acidity rather than from changes in metal dispersion alone.

9.7 Chemisorption

H_2 or CO chemisorption provides estimates of exposed metal surface and dispersion. Such measurements are particularly important when comparing catalysts with different supports because TEM-derived particle size does not necessarily correspond to the number of chemically accessible surface atoms.

Table 2. Characterization techniques and their principal contributions

Technique	Primary information
Wide-angle XRD	Crystalline phases, support structure, larger metal crystallites
SAXRD/SAXS	Mesopore ordering
N_2 adsorption–desorption	Surface area, pore volume, pore-size distribution
TEM/HRTEM	Particle size and morphology
HAADF-STEM	Highly dispersed noble-metal species
XPS	Surface oxidation state and electronic interaction
H_2-TPR	Reducibility and metal–support interaction

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Technique	Primary information
NH_3-TPD	Amount and strength of acid sites
Pyridine-IR	Brønsted/Lewis acidity
H_2/CO chemisorption	Accessible metal dispersion
ICP-OES/ICP-MS	Bulk metal loading

X. CATALYTIC APPLICATIONS

10.1 Selective oxidation of alcohols

Selective oxidation of alcohols to aldehydes and ketones is an important route to fine chemicals and pharmaceutical intermediates. Pd and Pt catalysts are particularly effective in aerobic oxidation.Mesoporous materials are advantageous for benzyl alcohol and substituted aromatic alcohols because their channels allow efficient diffusion of both alcohol and aldehyde products. Studies of Pd supported on different mesoporous silicas have demonstrated that mesostructure and pore connectivity can strongly influence oxidation rates through simultaneous changes in Pd dispersion and mass transport [11].Microporous zeolites can provide additional selectivity when substrates fit the pore dimensions. However, substituted aromatic alcohols may encounter restricted diffusion, particularly in medium-pore zeolites. For such molecules, hierarchical or mesoporous catalysts may therefore provide greater apparent activity.

10.2 Hydrogenation

Hydrogenation reactions are highly sensitive to metal particle size, support acidity and mass transport. Pt, Pd, Ru and Rh are all extensively used.For aromatic ketones or bulky carbonyl compounds, wide mesopores provide rapid access to metal sites. Ru dispersed over MCM-41 or SBA-15 can therefore be effective where complete hydrogenation requires repeated adsorption and hydrogen transfer.In microporous zeolites, confinement may modify adsorption geometry and product selectivity. Acid sites may additionally catalyse secondary transformations. The outcome can be desirable in tandem processes but detrimental when a single hydrogenation product is required.

10.3 Environmental catalysis

Small molecules such as CO, NO, NO_2 and light hydrocarbons can diffuse through many zeolite pore systems more easily than bulky organic substrates. Consequently, microporous supports are highly relevant to environmental catalysis.Pd- and Pt-containing zeolites benefit from high metal dispersion, ion-exchange stabilization and thermal resistance. Strong confinement can suppress nanoparticle growth during hydrothermal aging. Mesoporous supports remain useful when rapid gas transport and lower diffusion resistance are required.

10.4 Coupling reactions

Pd/SBA-15 systems have been extensively investigated in Suzuki, Heck and related C–C coupling transformations [10]. The mesopores accommodate Pd nanoparticles and facilitate access of relatively large aromatic reactants. Surface functionalization can reduce Pd leaching and improve recyclability.Microporous zeolites can provide stable Pd environments but may be less suitable for coupling reactions involving sterically demanding organic molecules unless external surface sites or hierarchical porosity are available.

XI. CATALYST DEACTIVATION AND STABILITY

Catalyst stability is an essential component of practical performance.

Sintering occurs when small metal particles migrate and coalesce. Mesopore walls restrict migration to some extent, whereas true zeolite encapsulation can provide much stronger physical confinement. Encapsulated noble metals have therefore shown notable resistance to sintering [7–9].

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Pore blockage is especially serious for microporous catalysts because relatively small deposits can obstruct an entire channel. Mesopores tolerate larger deposits before transport becomes severely restricted.

Coke formation is influenced by support acidity. Strongly acidic zeolites may promote oligomerization, condensation and cracking pathways that generate carbonaceous deposits. Pure silica SBA-15 and MCM-41 are less acidic and may exhibit lower coking tendencies in some organic transformations.

Metal leaching is important in liquid-phase reactions. Functionalized mesoporous supports and encapsulated zeolites can both improve metal retention, although the mechanisms differ.

Therefore, catalyst stability represents another trade-off: strong confinement improves metal retention, but excessive confinement can reduce reactant access.

XII. HIERARCHICAL MICRO–MESOPOROUS SUPPORTS: COMBINING THE ADVANTAGES

The intrinsic limitations of purely microporous zeolites have motivated the development of hierarchical materials containing secondary mesopores [12–14]. The design concept is straightforward:

Micropores provide:
confinement + acidity + shape selectivity
Mesopores provide:
rapid diffusion + large-molecule accessibility
Hierarchical micro–mesopores provide:
confinement + acidity + accessibility + improved transport.

Hierarchical zeolites can be synthesized by bottom-up templating or produced through post-synthetic treatments such as desilication. The additional mesopores shorten diffusion pathways and improve utilization of internal zeolite active sites while retaining important framework characteristics.

For noble-metal catalysts, hierarchical materials offer further advantages. Nanoparticles can be located in secondary mesopores, while smaller species interact with microporous domains. This creates the possibility of deliberately positioning different catalytic functions at different length scales. However, hierarchical materials must be designed carefully. Excessive introduction of mesoporosity can destroy crystallinity, reduce acidity or create uncontrolled external surface sites. The objective should therefore not be maximum mesopore volume but optimized connectivity between micro- and mesoporous domains.

XIII. CRITICAL PERSPECTIVE

A universal ranking of mesoporous and microporous supports is scientifically inappropriate because catalyst performance depends on the target reaction.

Mesoporous materials are generally preferable when bulky substrates are involved, rapid diffusion is essential, a large accessible metal surface is required or pore blockage must be minimized. These characteristics favour applications in selective oxidation, liquid-phase hydrogenation and fine-chemical synthesis. Microporous zeolites are particularly attractive when molecular shape selectivity, thermal stabilization, controlled active-site environments or metal–acid bifunctionality is required. They are therefore especially relevant to hydrocarbon transformations and small-molecule catalysis.A more meaningful selection principle is to choose the pore architecture according to the molecular dimensions, required reaction pathway, desired active-site environment, and dominant deactivation mechanism.

This principle shifts catalyst design from simple material selection toward reaction-specific pore engineering.

XIV. FUTURE PERSPECTIVES

Several directions are expected to dominate future development. First, catalyst design must progress from maximizing total metal dispersion toward engineering accessible active sites. The most useful metal atom is not necessarily the most highly dispersed one, but the one that remains accessible, stable, and electronically appropriate under reaction conditions. Second, controlled spatial positioning of noble metals will become increasingly important. Advanced

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synthesis should determine whether metal atoms reside at pore mouths, channel intersections, mesopore walls, zeolite cages or external surfaces.Third, single-atom and subnanometric noble-metal catalysts offer a route to dramatically improved atom efficiency. Zeolite frameworks are particularly suitable for stabilizing isolated species, although the relationship between atomic dispersion and long-term stability requires continued investigation.Fourth, hierarchical micro–mesoporous structures will remain important because they address the classical trade-off between confinement and accessibility.

Recent comprehensive analyses of hierarchical zeolites demonstrate their ability to improve mass transport while preserving the intrinsic catalytic properties of microporous frameworks [13,14].Fifth, operando characterization should increasingly replace conclusions based solely on ex situ measurements. Noble-metal particles can change oxidation state, coordination environment and morphology during catalysis. Techniques such as X-ray absorption spectroscopy, environmental TEM, operando DRIFTS and synchrotron scattering can reveal the structure of the true working catalyst.Finally, economic and sustainability pressures require lower noble-metal loadings, greater recyclability and longer catalyst lifetimes. Rational control of pore architecture can contribute directly to these goals by improving utilization of each metal atom.

XV. CONCLUSIONS

Mesoporous and microporous supports provide fundamentally different environments for supported noble-metal catalysts. Ordered mesoporous materials such as SBA-15 and MCM-41 combine high surface area, large pore volume and relatively unrestricted diffusion. Their channels can accommodate Pt, Pd, Ru, and Rh nanoparticles while maintaining accessibility to bulky organic reactants. These properties make mesoporous supports particularly useful for selective oxidation, hydrogenation, coupling and other fine-chemical transformations. Microporous zeolites such as ZSM-5, ZSM-22, Beta and Y offer stronger confinement, tunable acidity, ion-exchange capacity and molecular shape selectivity. They can stabilize isolated ions, single atoms, clusters, and encapsulated nanoparticles and substantially improve resistance to sintering. Their principal limitation is restricted intracrystalline diffusion, particularly for large organic substrates. Mesoporous supports primarily maximize accessibility and transport, whereas microporous supports maximize confinement, stability and molecular recognition. Neither characteristic is universally preferable. Optimal performance requires matching pore architecture to the molecular size of the reactant, mechanism of the reaction, and desired active-site environment. The most promising direction is the development of hierarchical micro–mesoporous materials that combine zeolitic confinement and acidity with secondary transport pathways. Future catalyst development should increasingly emphasize the relationship: Pore architecture → metal location → accessible dispersion → metal–support interaction → molecular transport → activity, selectivity and stability. Such pore–metal–molecule engineering provides a rational basis for developing highly active, selective, stable and resource-efficient noble-metal heterogeneous catalysts.

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