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Molecular Metal Catalysts on Supports: Organometallic Chemistry Meets Surface Science

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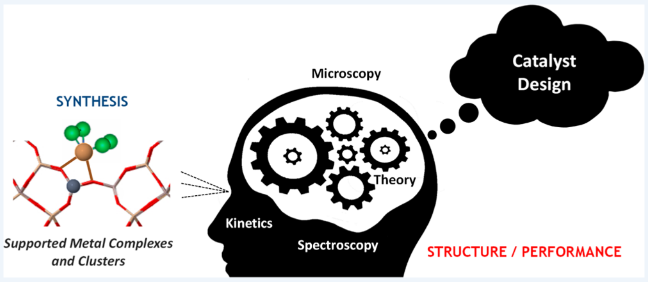

CONSPECTUS: Recent advances in the synthesis and characterization of small, essentially molecular metal complexes and metal clusters on support surfaces have brought new insights to catalysis and point the way to systematic catalyst design. We summarize recent work unraveling effects of key design variables of site-isolated catalysts: the metal, metal nuclearity, support, and other ligands on the metals, also considering catalysts with separate, complementary functions on supports. The catalysts were synthesized with the goal of structural simplicity and uniformity to facilitate incisive characterization. Thus, they are essentially molecular species bonded to porous supports chosen for their high degree of uniformity; the supports are crystalline aluminosilicates (zeolites) and MgO. The catalytic species are synthesized in reactions of organometallic precursors with the support surfaces; the precursors include $M(L)_2(acetylacetonate)_{1-2}$, with M = Ru, Rh, Ir, or Au and the ligands L = C_2H_4, CO, or CH_3. $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ are used as precursors of supported metal clusters, and some such catalysts are made by ship-in-a-bottle syntheses to trap the clusters in zeolite cages.

The simplicity and uniformity of the supported catalysts facilitate precise structure determinations, even in reactive atmospheres and during catalysis. The methods of characterizing catalysts in reactive atmospheres include infrared (IR), extended X-ray absorption fine structure (EXAFS), X-ray absorption near edge structure (XANES), and nuclear magnetic resonance (NMR) spectroscopies, and complementary methods include density functional theory and atomic-resolution aberration-corrected scanning transmission electron microscopy for imaging of individual metal atoms. IR, NMR, XANES, and microscopy data demonstrate the high degrees of uniformity of well-prepared supported species. The characterizations determine the compositions of surface metal complexes and clusters, including the ligands and the metal−support bonding and structure, which identify the supports as ligands with electron-donor properties that influence reactivity and catalysis.

Each of the catalyst design variables has been varied independently, illustrated by mononuclear and tetranuclear iridium on zeolite HY and on MgO and by isostructural rhodium and iridium (diethylene or dicarbonyl) complexes on these supports. The data provide examples resolving the roles of the catalyst design variables and place the catalysis science on a firm foundation of organometallic chemistry linked with surface science. Supported molecular catalysts offer the advantages of characterization in the absence of solvents and with surface-science methods that do not require ultrahigh vacuum.

Families of supported metal complexes have been made by replacement of ligands with others from the gas phase. Spectroscopically identified catalytic reaction intermediates help to elucidate catalyst performance and guide design. The methods are illustrated for supported complexes and clusters of rhodium, iridium, osmium, and gold used to catalyze reactions of small molecules that facilitate identification of the ligands present during catalysis: alkene dimerization and hydrogenation, H-D exchange in the reaction of H_2 with D_2, and CO oxidation. The approach is illustrated with the discovery of a highly active and selective MgO-supported rhodium carbonyl dimer catalyst for hydrogenation of 1,3-butadiene to give butenes.

1. MOLECULAR CATALYSIS ON SUPPORTS

The typical industrial catalyst is a solid that is stable and readily separated from fluid-phase products and consists of nanoparticles of a transition metal, oxide, or sulfide dispersed on the internal surface of a porous high-area support. The catalytically active species are nonuniform, minority structures that are challenging to identify. Surface scientists simplified matters by using single crystals, cleaning the surfaces under ultrahigh vacuum (UHV), but understanding of catalysts in UHV is limited by the lack of stability of most reactive surface ligands. In contrast, soluble catalysts are more nearly uniform and readily identified; they are molecular, and researchers often discover better ones by varying the metal, ligands, and other design variables (Table 1). Here we describe research bridging surface science and molecular chemistry, but without the

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limitations of UHV or the complications of solvents. We describe molecular catalysts bonded to supports.

This field has deep roots; early researchers[1,2] investigated anchored organometallics, focusing on alkene polymerization catalysis. Industrial polymerization catalysts today include silica-supported mononuclear chromium complexes[3] and metallocenes.

Understanding of most supported molecular catalysts is hampered by the nonuniformity of the surface species and the limited characterization tools. These catalysts have been reviewed,[4] and we skip over early work, focusing on recent well-defined examples. The field is drawing heightened attention because

- crystalline supports presenting nearly uniform surface sites facilitate characterization;
- characterization tools have improved markedly;
- quantitative understanding of metal−support bonding and structure is emerging;
- well-defined supported catalysts incorporating metals of industrial interest have emerged.

Supports differentiate our topic from homogeneous organometallic catalysis. Supports are macroligands that play any of the roles of ligands in solution catalysis, and more; supports stabilize site-isolated catalytic species and limit their aggregation into crystallites. Supports also provide sites that complement primary catalytic sites by activating nearby reactants to form intermediates that migrate to the primary sites.

When supported catalysts consist of mononuclear metal complexes or small clusters, the metal−support interactions are strong and markedly influence the chemistry. But when supported species are bulk-like, the support is just a platform that barely affects the chemistry, and then surface science is a foundation for understanding them. In contrast, when the supported species are essentially molecular, the foundation is organometallic chemistry.

Table 1. Design Variables for Classes of Metal Catalysts

design variable	molecular organometallic catalysts in solution	bulk supported metal catalysts	molecular metal catalysts on supports
metal	in general, the metal affects catalyst performance; demonstration of effects of the metal requires isostructural species and often challenging syntheses.		
ligands	well-defined, simple, and flexible; easily characterized; predictable electron transfer with metal; affect steric accessibility; enable enantioselectivity; include reaction intermediates during catalysis	ill-defined surface species, often residues from metal salt precursors (e.g., chlorides or nitrates); lack of uniformity hinders accurate characterization; the support acts weakly as a ligand for the few metal atoms at the metal particle periphery	as in organometallic catalysis in solution, and the ligands include the support; the support effect is maximized when the metal species are smallest
metal nuclearity	from one to a few metal atoms per catalytic unit; variable nuclearities accomplished through changes in number and class of ligands and synthesis conditions; during catalysis, removal or exchange of ligands may lead to change in nuclearity	typically particles with thousands of atoms or more, most of them inaccessible for catalysis; different domains on metal particles (e.g., terrace, step, or corner sites) often perform differently; roles of these sites often blurred by intrinsic nonuniformity of particles	as in organometallic catalysts in solution, with the support influencing the structure and stability of the sites; the support may facilitate conversion of one species into another in cluster formation/breakup processes
electron density/ oxidation state	often early or late transition metals in a well-defined (often high) oxidation state; electron-counting rules apply	aggregated zerovalent metal (particles) or metal oxides or sulfides at surface, depending on species in contact with particles and variable from position to position	as in organometallic catalysis in solution, but common supports are oxides, which are unlike most ligands in solution organometallic catalysis
reaction conditions	solvent influences reactivity; often limited to mild conditions because of low stability of the molecular species and expense of high pressure required to keep components in liquid phase	solvent usually avoided; wide range of temperatures and pressures applicable; high temperature attainable at low pressures, a major economic and technological advantage	stability enhanced by the support may broaden the range of conditions compared with those of organometallic catalysis in solution, but stability limitations are significant
complementarity of catalytic species	cooperation between various metal atoms directly bonded to each other or connected through ligands (as in pincer catalysis), or just nearby in solution	cooperation between metal atoms in alloys or bimetallic; metal/support boundaries (a small fraction of the total sites); widely separated species may be linked in catalysis via mobile (spilled-over) intermediates	concepts underlying both catalysis by organometallics in solution and bulk materials on supports pertain (see left); opportunity for juxtaposition of stably anchored catalytic sites

2. UNIFORMITY OF SUPPORTED CATALYSTS: KEY TO FUNDAMENTAL UNDERSTANDING

2.1. Choice of Metal Precursors and Supports

Our supports are crystalline porous materials that offer nearly uniform, well-defined surfaces. Most are aluminosilicates, zeolites, and another is a prototypical metal oxide, MgO, which is less uniform than zeolites. The supports are high-area powders like those used in industry. They consist of light atoms (Al, Mg, Si, O, H) and thereby provide a great advantage for characterization of heavy metals on their surfaces by high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM), because then *Z*-contrast enhancement allows imaging of individual heavy metal atoms.[5]

We emphasize rhodium, iridium, and gold, because they catalyze many reactions of alkenes, alkynes, CO, etc., and can be synthesized as stable mononuclear metal complexes and clusters.[6] The precursors of the supported species are not the metal salts used for industrial catalysts (because they give nonuniform structures), but rather organometallic compounds that react cleanly with supports. Typical precursor ligands are acetylacetonate (acac) because metal acac complexes react with supports to make metal−surface-oxygen bonds, liberating acac without removal of the other ligands. Thus, the catalysts are synthesized from $M(L)_2(acac)_{1-2}$, with M = Ru, Rh, Ir, or Au and the ligands L = C_2H_4, CO, or CH_3. The precursor reacts with a support slurried in *n*-pentane.[7−9] Supported metal

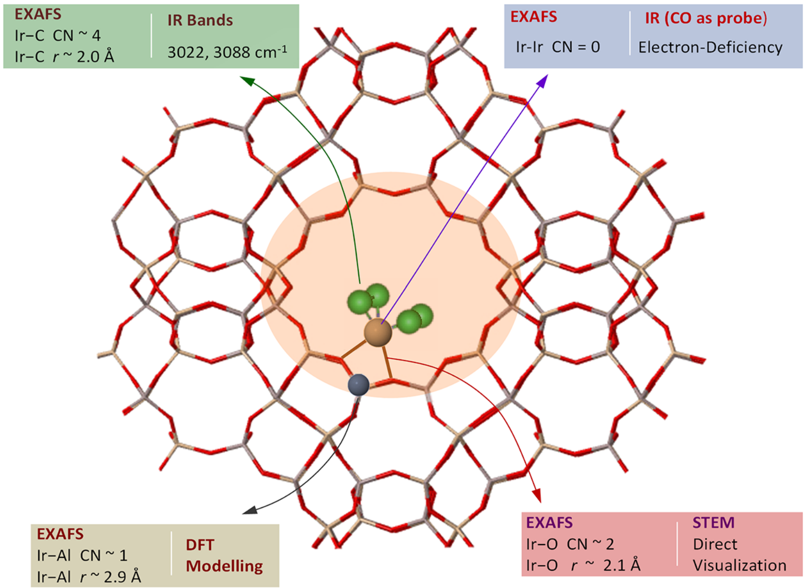

Figure 1. Iridium diethylene in zeolite Y characterized by various techniques.[5,8,13]

clusters are often synthesized from precursors with metal frames incorporating carbonyl ligands, but syntheses with preformed clusters do not work with most zeolite supports because the narrow zeolite apertures exclude them. Instead, surface-mediated reactions of small mononuclear metal complex precursors are used in ship-in-a-bottle syntheses.

2.2. Spectroscopy, Microscopy, and Theory: Evidence of Uniform Metal Sites on Supports

Spectroscopy provides structural information averaged over a sample, and the typical surface hosts a smear of species, with broad spectral peaks. When support surfaces are nearly uniform, however, nearly uniform anchored species facilitate precise spectroscopic characterization. Structures of Ir(C_2H_4)$_2$ and Rh(C_2H_4)$_2$ complexes on HY zeolite, for example (Figure 1, Table 2), are based on IR and EXAFS spectra identifying the ligands, EXAFS spectra determining the metal−support-oxygen coordination numbers and distances, and DFT calculations characterizing bond strengths and ligand dissociation energies.[6] The metals are present at Al sites, being cationic and replacing protons of OH groups, which react to form Hacac. IR spectra of the metal complexes probed with CO confirm the locations at acidic Al sites, with experimental ν_{CO} frequencies matching calculated values.[7] Families of isostructural surface complexes allow determination of the roles of various supports as ligands.

CO is a good probe of metal sites because it bonds strongly and gives strong IR signals. Thus, Rh(CO)$_2$ on zeolite HY at Al sites has sharp ν_{CO} IR bands demonstrating the uniformity (fwmh < 5 cm^{-1}). The breadth of ν_{CO} bands is the easiest criterion to gauge the uniformity of supported species. However, CO may be a noninnocent probe, changing the structures of the metal species.

Evidence of the high degree of uniformity of rhodium complexes on HY zeolite was further demonstrated by ^{13}C CP MAS NMR spectroscopy. The resonance broadened out completely at one temperature, demonstrating a balance of the effects of ^{1}H−^{13}C dipolar decoupling and random anisotropic reorientation of the ^{1}H−^{13}C bond vector, thus indicating a dynamic uniformity of the environment of the ^{13}C atoms and implying the structural uniformity of the rhodium sites.[10] XANES spectra provide additional evidence of the uniformity of supported species when spectra recorded during treatments show isosbestic points demonstrating the conversion of one species to another. Furthermore, STEM enables visualization of individual heavy metal atoms on supports, demonstrating their site isolation and in zeolites possibly determining their crystallographic locations; thus, gold complexes in zeolite NaY (Figure 2A) are present in only two locations.[11]

The images also help determine metal−support interface structures. For example, the structure of Os(CO)$_2$ on MgO was determined by STEM, IR, and EXAFS data (Figure 2B). The Os atoms are on average widely separated from each other; each bonds to three or four O atoms of the support at Mg vacancies.[12]

Essentially uniform supported metal complexes are nearly optimal for investigation by theory, and DFT calculations agree well with experiment (Figure 1).[7]

3. METAL−LIGAND INTERACTIONS IN SUPPORTED METAL COMPLEXES: EFFECT OF SUPPORTS ON ACTIVATION OF MOLECULES FROM THE FLUID PHASE

Ligands remaining on metals after precursor anchoring can be replaced by reactive gas-phase ligands. In flow reactors, the reactant stream is a sweep gas that removes dissociated ligands to overcome equilibrium limitations.[7] HY zeolite-supported rhodium and iridium complexes exchange CO, C_2H_4, H, D, and N_2 ligands.[7,13] Although the ligand replacement process is sometimes impractically slow, the method is general and leads to new structures (Table 2).[7,13]

Metals in complexes on HY zeolite are more electron-deficient than those on MgO, because the zeolite is an electron-withdrawing ligand and MgO the reverse.[14,15] The reactivities of the supported species accordingly depend on the support. With added CO, iridium on HY zeolite accommodates three CO ligands but on MgO only two.[13] In mixtures of CO and ethylene, zeolite-supported iridium bonds to both[13] but MgO-supported iridium only to CO. The replacement of CO by C_2H_4 in supported Ir(CO)$_2$ or Rh(CO)$_2$ is extremely slow on MgO but fast on the zeolite.[7,13]

Table 2. Supported Molecular Metal Species and Structure and Performance Characteristics

metal complex catalyst precursor (support ligands not shown)	support	information provided by EXAFS spectroscopy[a]		IR bands characteristic of ligands bonded to metal (band locations in cm^{-1})[b]	key observations regarding structure, reactivity, and catalysis
		N (M−M)	R (M−M), Å		
$Ir(C_2H_4)_2$	HY zeolite, MgO			3022 and 3088 (HY zeolite); 3001 and 3032 (MgO)	Species on HY zeolite 24 times more active as catalyst than on MgO for ethylene hydrogenation
$Rh(C_2H_4)_2$	HY zeolite, MgO			3084, 3060, and 3016 (HY zeolite); 3059 and 2999 (MgO)	Catalytic dimerization of ethylene on HY zeolite but hydrogenation on MgO (both in presence of H_2)
$Ir_4(C_2H_5)_{3-6}$	HY zeolite, MgO	3.1 (HY zeolite); 2.9 (MgO)	2.67 (HY zeolite); 2.73 (MgO)	2964, 2936, 2876, and 2854	Species on HY zeolite 6 times more active catalytically for ethylene hydrogenation than on MgO
$Rh_{2-4}(C_2H_5)_3$	HY zeolite	1.9	2.70	2964, 2933, 2878	Selective for ethylene hydrogenation catalysis
$Rh_2(C_2H_5)_2$	MgO	1.0	2.73	2963, 2924	60-fold increase in ethylene hydrogenation activity compared with single-atom complexes
$Rh_2(CO)_6$	MgO	1.0	2.73	1853, 1893, 1959, 2001, 2025, and 2074	Catalytically selective for partial hydrogenation of 1,3-butadiene
$Os(CO)_2$	MgO			2009, 1911	Metal/support interaction resolved by HAADF-STEM
$Rh(N_2)_2$	HY zeolite			2244, 2218	Experimental structure confirmed with DFT calculations

[a] N and R, metal−metal coordination numbers and bond lengths, respectively, determined by EXAFS spectroscopy. [b] Location stated at the maximum intensity of each IR peak.

The bonding of hydrogen to iridium and rhodium resulting from reaction with gas-phase H_2 depends on the support and other ligands.[13,14,16] Mononuclear electron-rich iridium and rhodium on MgO present higher barriers for metal hydride formation than the isostructural complexes on HY zeolite. Ethylene limits the interaction of the metal with H_2, but the effect is mitigated by an electron-withdrawing support.[13,14] CO is a stronger inhibitor of H_2 activation than ethylene. Although $Ir(CO)_2$ and $Rh(CO)_2$ on MgO are reactive for H_2 dissociation, these complexes on HY zeolite are active for catalytic H−D exchange in the $H_2 + D_2$ reaction.[13]

The foregoing statements also largely hold true when the catalytic species are metal clusters, but investigations of metal−ligand bonding are less straightforward for clusters than complexes. An exception is rhodium dimers on MgO;[17] CO is present both as terminal and as bridging ligands, with the latter more weakly bonded[17] and readily exchanged with alkenes, opening the door to selective catalysis by metal centers that are only partially blocked by other ligands.[17]

4. INTERCONVERSION OF SUPPORTED METAL COMPLEXES AND CLUSTERS

The interaction of a reductive gas like H_2 with a supported metal complex weakens the metal−support bonds, leading to metal migration and metal−metal bond formation (cluster formation), which is reversed, for example, with CO or ethylene as an oxidizing agent. Supported mononuclear and tetranuclear iridium are interconverted in stoichiometrically simple reactions, allowing ship-in-a-bottle synthesis of Ir_4 clusters[18] (or Ir_6 clusters) in zeolite cages.

Hydrogen accelerates the sintering of supported metal catalysts, leading to crystallite formation. We focus not on crystallites but rather on small metal clusters that are bonded to supports through most of their metal atoms. Ligands other than the support are also generally present; bare metal clusters are so reactive that they pick up hydride ligands from support OH groups via reverse hydrogen spillover.[19]

Spectra and images of samples reduced with H_2 elucidated the first steps of metal−metal bond formation, unravelling the transformation of $Rh(C_2H_4)_2$ (and $Ir(C_2H_4)_2$) into metal clusters.[20,21] Dissociation of H_2 on the metal forms metal hydrides;[20,21] then hydrogenation of ethylene ligands and breaking of metal−support-oxygen bonds induce metal migration and cluster formation. Because rhodium and iridium complexes activate hydrogen faster on HY zeolite than on MgO, clusters form faster on the zeolite, provided that reducible ligands are present.[20]

$Rh(CO)_2$ complexes are stable on HY zeolite in H_2 at temperatures up to 423 K, but the onset temperature for cluster formation on MgO is only 353 K, although rhodium activates H_2 faster on the zeolite than on MgO.[20] CO is a relatively unreactive ligand in complexes on either support. The following stability pattern emerged: HY zeolite-supported $Rh(CO)_2 \gg$ MgO-supported $Rh(CO)_2 >$ MgO-supported $Rh(C_2H_4)_2 >$ HY zeolite-supported $Rh(C_2H_4)_2$. Weakening of the M−O bonds in the latter two is facilitated by the facile H_2-induced formation of coordinatively unsaturated, partially hydrogenated $Rh(C_2H_5)_2$ species.

The stoichiometries of cluster formation and the structures of the clusters depend on the metal, support, and other ligands. Supported $Ir(C_2H_4)_2$ is cleanly converted into tetrairidium clusters in H_2 at 353 K (some hydrocarbon ligands remain), on either HY zeolite[18] or MgO.[14] Tetrairidium cluster formation

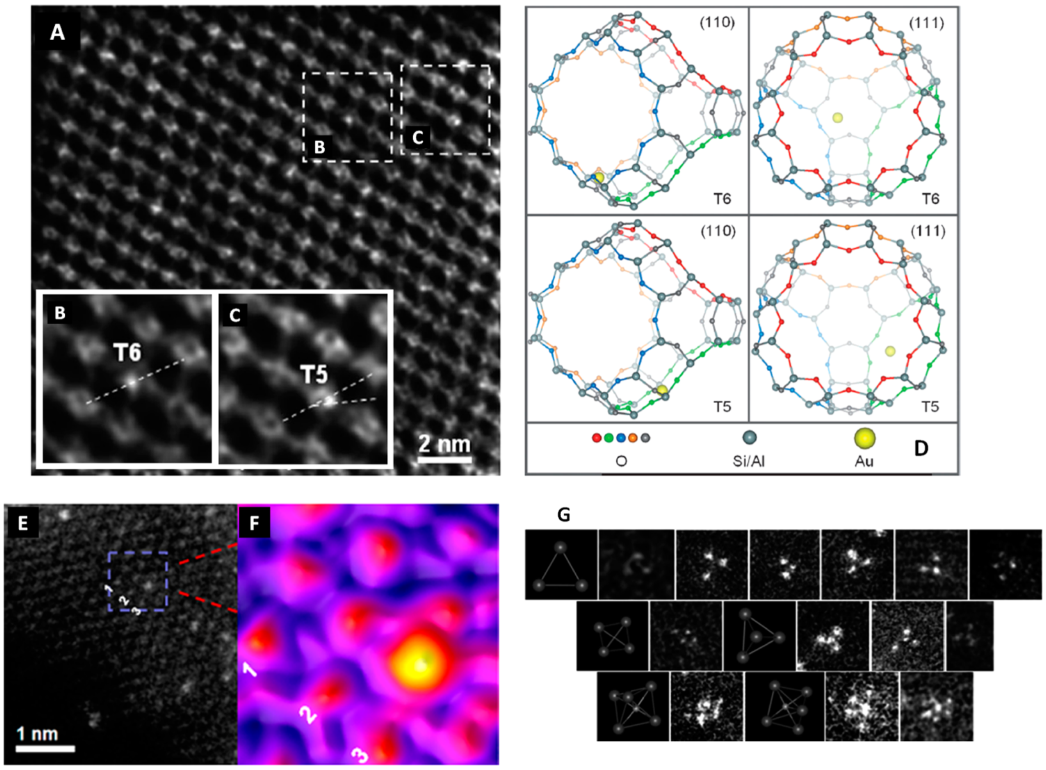

Figure 2. (A) Au atoms in mononuclear complexes at two positions (B, C) in NaY zeolite. (D) T5 and T6 positions of NaY zeolite. Adapted with permission from ref 11. Copyright 2012 Wiley VCH. (E) $Os(CO)_2$ complexes on MgO(110) and the corresponding image intensity map (F). (G) Various osmium clusters on MgO with nuclearities resolved by STEM. Adapted with permission from ref 12. Copyright 2012 American Chemical Society.

takes place by a reversible, stoichiometrically simple reaction demonstrated by XANES isosbestic points.[18] In contrast, in H_2, $Rh(C_2H_4)_2$ on the zeolite gives a mixture of small clusters,[22,23] whereas $Rh(C_2H_4)_2$ on MgO is converted precisely into rhodium dimers.[17]

Mononuclear osmium carbonyl complexes are converted into clusters when metal migration occurs in the presence of a ligand that stabilizes Os–Os bonds. Thus, $Os(CO)_2$ on MgO gives $[Os_{10}C(CO)_{24}]^{2-}$ (among others, with three, four, and five Os atoms); STEM images determine the metal frames (Figure 2).[24]

Small iridium and rhodium clusters are oxidatively fragmented with gas-phase CO[20] or C_2H_4[18,22,23] to give mononuclear metal complexes on acidic solids such as Al_2O_3, TiO_2, and H-form zeolites. When the metal is bonded to labile ligands such as ethylene, ethyl, or hydride, the balance in the reversible interconversion of supported complexes and clusters can be tuned by the gas-phase H_2/C_2H_4 ratio.[18,23] Spectra of HY zeolite-supported $Ir(C_2H_4)_2$ complexes in $H_2 + C_2H_4$ at 353 K show that they remain when the C_2H_4/H_2 molar ratio is 4:1 but instead form tetrairidium when the ratio is <1.[18] The dependence of structure on reaction environment provides levers for tuning catalytic properties.

In contrast, on the basic MgO, structures approximated as $Rh_2(CO)_6$ are stable.[17] These were synthesized from rhodium dimers incorporating ethyl and hydride ligands by reaction with CO.[17] These dimers are surprisingly stable in this oxidizing gas in the absence of H_2, although the Rh_2 carbonyl unit is commonly regarded as unstable.[25]

The process of bimetallic cluster formation in H_2 was followed spectroscopically with $Os_3(CO)_{12}$ and $Ru_3(CO)_{12}$ on MgO as the temperature increased.[26] The sequence of reactions is (a) partial decarbonylation of the ruthenium clusters, (b) scission of Ru–Ru bonds, (c) migration of ruthenium species on the surface, (d) formation of larger ruthenium clusters, (e) partial decarbonylation of osmium clusters, (f) migration of osmium species on the surface, and (g) formation of osmium clusters simultaneously with bimetallic clusters.

The noble metals referred to above are easily reduced and largely lacking in stability in the form of molecular species at temperatures higher than about 370 K. In contrast, complexes and clusters of metals of groups 5, 6, and 7 on supports are stable at temperatures hundreds of degrees higher. For example, trirhenium clusters on γ-Al_2O_3 catalyzed the conversion of methylcyclohexane with H_2 at 733 K and remained unchanged in nuclearity after catalysis.[27] Metals with oxophilic character may offer stability combined with unanticipated catalytic properties for numerous reactions and offer rich opportunities for catalyst discovery.

5. CATALYST PERFORMANCE ELUCIDATED ON THE BASIS OF ORGANOMETALLIC CHEMISTRY PRINCIPLES

Data characterizing metal complexes and clusters as catalysts for reactions involving ligands such as hydride, alkene, and alkyl allow resolution of the effects of catalyst design variables (Table 1). We illustrate effects of changing the metal, metal nuclearity, support, and other ligands. We emphasize an implicit oversimplification in our statement: keeping some components of the catalyst the same while changing others means keeping the unchanged components the same in the *catalyst precursor*, not necessarily in the reactive intermediates. This point emphasizes the importance of determining catalyst structure during operation. Thus, we refer to spectra of functioning catalysts but emphasize that this approach is limited too, because not all species in a catalytic cycle are spectroscopically detectable. Theory is needed to fill the gaps.

Data characterizing the catalytic reactions of light alkenes in the presence of H_2 were recorded under mild conditions to minimize changes in the catalytic structures. Typically, conversions and selectivities were measured at 1 bar, 298–353 K, and various partial pressures of ethylene and H_2. Differential conversions were measured to determine reaction rates (turnover frequencies, TOF) in flow reactors. TOFs were calculated per total metal atom, assuming that all of them were accessible for catalysis.

5.1. Catalyst Performance Affected by the Support as a Ligand

The formation of a metal–reactant bond is usually a prerequisite for catalysis. The support as a ligand affects how reactants interact with the metal. Consider a family of catalysts consisting initially of $Ir(C_2H_4)_2$ and $Rh(C_2H_4)_2$ on HY zeolite or MgO.[7,8,13] These isostructural complexes allow resolution of the metal and support effects. At 298 K and 333 mbar C_2H_4 and 666 mbar H_2, the TOF values with mononuclear iridium were 0.71 and 0.03 s^{-1} when the supports were zeolite HY and MgO, respectively,[14] with ethane as the main product (with *n*-butene traces).[14,28] Similarly, data were obtained for Ir_4 on γ-Al_2O_3 and on MgO; with Ir_4/γ-Al_2O_3, the TOF for ethylene hydrogenation was 0.23 s^{-1} at 295 K and ethylene and H_2 partial pressures of 53.3 mbar and 133.3 mbar, respectively; with Ir_4/MgO, the TOF was 0.052 s^{-1}.[29]

Supports also affect catalyst selectivity. $Rh(C_2H_4)_2$ on MgO forms a catalyst that is 100% selective for ethylene hydrogenation, but with the zeolite as the support, ethylene dimerization predominates at 298 K, 148 mbar of H_2, and 428 mbar of C_2H_4 (and the zeolite without rhodium is inactive for dimerization under these conditions).[23,30] The latter result is intriguing because rhodium is typically inactive for C–C bond formation unless labile ligands such as chloride are present.[30] New dimerization catalysts such as these may be important in light of the commercial production of light alkenes from natural gas.

5.2. Catalyst Performance Affected by Metal Nuclearity

$Ir(C_2H_4)_2$ on HY zeolite (and MgO) was treated in H_2 to give Ir_4 clusters incorporating ethylene, ethyl, and ethylidyne ligands.[18] The effect of metal nuclearity on catalysis was determined at 298 K and partial pressures of C_2H_4 and H_2 of 333 and 666 mbar, respectively. With the MgO support, the TOF increased from 0.03 to 0.18 s^{-1} as the iridium nuclearity increased from 1 to 4;[14] with the zeolite, the increase was from 0.71 to 0.86 s^{-1}.[14] The data thus resolve the effects of the support and metal nuclearity and show that the effect of nuclearity is less when the support is electron-withdrawing.

Neighboring metal centers facilitate H–H bond scission, and with MgO as the support, conversion of mononuclear rhodium complexes to dimers increased the catalytic activity for ethylene hydrogenation 60-fold at 298 K with a H_2/C_2H_4 molar ratio of 4.[17] Effects of metal nuclearity were also determined with Ir_4 and Ir_6:[31] with Ir_4/γ-Al_2O_3, the TOF was 0.2 s^{-1} at 288 K and 66 mbar of C_2H_4 and 400 mbar of H_2, but with Ir_6/γ-Al_2O_3, the TOF was only about 0.02 s^{-1}. These observations demonstrate a limitation of the commonly stated surface-science-based inference that alkene hydrogenation is a structure-insensitive reaction. This designation does not apply to metal frames consisting of only a few atoms, which should be understood on the basis of molecular principles.

The effect of metal nuclearity on catalytic selectivity is illustrated by MgO-supported rhodium catalysts. Regulation of the H_2 dissociation activity emerged as a key challenge in the design of a selective 1,3-butadiene hydrogenation catalyst; high activity for H_2 dissociation boosts routes to the undesired *n*-butane at the expense of 1-butene.[16] Thus, when rhodium complexes were converted to dimers, the TOF for 1,3-butadiene hydrogenation increased from 0.007 to 0.014 s^{-1} at 298 K and H_2 and diene partial pressures of 980 mbar and 20 mbar, respectively, and the selectivity to *n*-butene decreased from 91.5 to 82.4% at diene conversions <15%.[16]

Although mononuclear zeolite HY-supported rhodium complexes catalyze predominantly ethylene dimerization in H_2 at 298 K, small rhodium clusters (average Rh–Rh coordination number ≈ 2) selectively catalyze hydrogenation.[23]

5.3. Catalyst Performance Affected by Ligands Other than the Support

CO is a catalyst poison, and when the ethylene ligands in $Rh(C_2H_4)_2$ (or $Ir(C_2H_4)_2$) on MgO were replaced with CO, the catalytic activity for alkene hydrogenation and the H–D exchange reaction ceased.[13,16] Different behavior was observed with iridium complexes on zeolite HY, because then both ethylene and CO bonded to the metal, and the catalyst was active for the H–D exchange reaction, although not for ethylene hydrogenation.[13]

CO ligands are more easily replaced by alkenes when (a) the metal is present as small clusters rather than mononuclear complexes and (b) the CO ligands are bridging. Replacement of such ligands by 1,3-butadiene in MgO-supported $Rh_2(CO)_6$ led to catalytic activity for hydrogenation,[16] and high selectivities to *n*-butenes were achieved (>99%) at conversions as high as 97%. The catalyst loses selectivity only at the highest diene conversions (>97%), because then the excess of butenes allows them to bond preferentially to the metal sites over 1,3-butadiene. This result is potentially significant for industrial application because diene impurities diminish the quality of polymers formed from 1-butene.

A subtle control of the catalytic activity of the metal centers on Ir_4 was recently found to be exerted by three bulky calixarene phosphine ligands nearly enveloping the metal core, which also incorporated CO ligands. CO ligands on the basal plane of Ir_4 supported on silica were reversibly removed by thermal desorption, but because of electronic effects (demonstrated by DFT calculations), ethylene did not bond to these sites and was not converted catalytically with H_2.[32] But when CO ligands were tweezed out of apical Ir sites by oxidation with trimethylamine N-oxide, these sites became reactive with ethylene and catalytically active for ethylene hydrogenation. The deft control of reactivities of single-metal-atom sites in a cluster calls to mind enzyme-like chemistry.

5.4. Catalyst Performance Affected by the Metal

The following results demonstrate the influence of changing the metal without changing the metal nuclearity, support, and other ligands. MgO-supported iridium and rhodium complexes and clusters all selectively catalyze ethylene hydrogenation in H_2 + C_2H_4 mixtures,[14,17,33] but Rh_6 clusters are an order of magnitude more active than Ir_6,[34] and $Ir(C_2H_4)_2$ gives a catalyst more active (TOF = 0.030 s^{-1}[14]) than $Rh(C_2H_4)_2$ (0.019 s^{-1}[17]) in excess H_2. The effect of the metal on catalytic

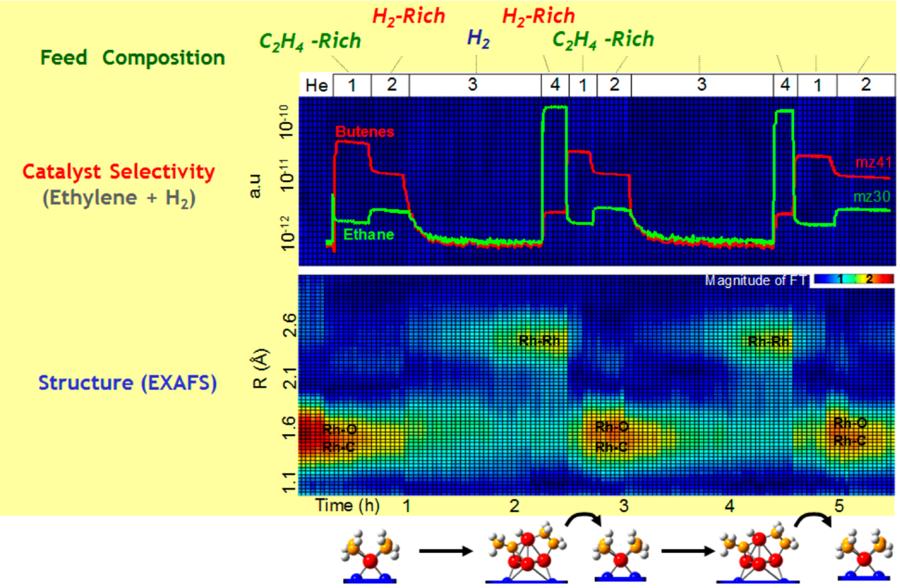

Figure 3. Changes in selectivity of a catalyst initially containing $Rh(C_2H_4)_2$ supported on HY zeolite as the feed composition (ethylene and H_2) was changed cyclically and the structure of the active sites tracked with EXAFS spectroscopy. In the bottom panel, the horizontal axis represents time on stream, the vertical axis represents the Rh−backscatterer distance, and the colors represent the magnitudes of various contributions (change from red to yellow to green to blue shows a decrease in intensity of the contribution). Adapted with permission from ref 23. Copyright 2011 American Chemical Society.

performance is thus flipped depending on the metal nuclearity, consistent with theory, which points to iridium complexes as more reactive for H_2 dissociation than rhodium complexes (unpublished work with M. Chen and D. A. Dixon) and the greater effect of neighboring metal centers on the hydrogenation activity when the metal is rhodium[17] rather than iridium.[14]

The metal also affects the catalytic performance when the support is HY zeolite—but now in terms of selectivity, provided that the metal is in site-isolated complexes. Iridium complexes on this support catalyze predominantly hydrogenation of ethylene in the presence of H_2 at 298 K,[14,28] whereas the isostructural rhodium complexes catalyze predominantly dimerization.[23,30]

5.5. Spectra of Working Catalysts Facilitate Understanding of Performance

Elucidation of catalytic chemistry is facilitated by spectroscopic identification of reaction intermediates and the inference of rate-determining steps. In ethylene hydrogenation with $Ir(C_2H_4)_2$ and $Rh(C_2H_4)_2$ as precursors on MgO, EXAFS spectra of working catalysts demonstrate that the most stable species are $M(C_2H_4)_2$ (M = Rh or Ir), consistent with the slow reaction of H_2 with π-bonded ethylene ligands to form ethyl ligands.[14,20] Moreover, data characterizing the H_2 dissociation activity (in the reaction of H_2 + D_2) and the ethylene hydrogenation activity of MgO-supported iridium complexes and Ir_4 clusters correlate well;[14] the rate of ethylene hydrogenation is greater when the catalytic species incorporate M−M bonds, with neighboring metal centers favoring H_2 dissociation. H_2 dissociation is thus rate determining, explained by the high electron density of each metal on this electron-donor support and the strong metal−ethylene interactions.[14]

However, because HY zeolite is a weaker electron-donor than MgO, the supported iridium complexes are more electron-deficient on the former, which implies that the mononuclear iridium complex has a greater capacity for ligands, a greater activity for H_2 dissociation, and thus a greater activity for ethylene hydrogenation. EXAFS and IR spectra indicate that $Ir(C_2H_5)_2$ species have the longest lifetimes in the ethylene hydrogenation cycle,[14] which suggests that the H_2 activation step is not rate-determining.

In contrast, the effect of the support on the hydrogenation activity is less when the catalytic species are Ir_4 clusters rather than mononuclear iridium complexes, although both catalyze H_2 dissociation.[14] The weaker influence of the support in the case of Ir_4 is consistent with observations that H_2 dissociation is not rate-determining and the electron density is delocalized over the Ir_4 unit.[14]

$M(C_2H_4)_2$ complexes (M = Rh or Ir) are reversibly converted into metal clusters in mixtures of ethylene + H_2.[23,28] With rhodium, the conversion of one species into another drastically changes the catalyst selectivity. EXAFS spectra determining changes in the Rh−Rh, Rh−C, Rh−O, and Rh−Al coordination numbers and distances indicate the effects of H_2 and C_2H_4 partial pressures on the rates of ethylene dimerization and hydrogenation,[23] demonstrating that when rhodium complexes are stable, dimerization prevails and when clusters are stable, hydrogenation prevails (Figure 3).[23] In catalysis by rhodium complexes on zeolite HY, the metal and zeolite Al sites work in concert in the C−C bond formation.[30]

MgO-supported $Rh(C_2H_4)_2$ complexes in H_2 + 1,3-butadiene showed increasing hydrogenation activities as small rhodium clusters formed.[16] When gold complexes on CeO_2 were converted to the smallest gold clusters, the catalytic activity for CO oxidation increased dramatically.[35] The activities of MgO-supported gold catalysts for CO oxidation depend on the CO/O_2 ratio, with the activity correlated with the amount of cationic gold, indicated by XANES spectra of working catalysts.[36]

All these results underline the subtlety of the molecular surface organometallic chemistry, with the effects of metal nuclearity and support chemistry being intricately coupled, so that elucidation of the chemistry benefits greatly from systematic variations of simple, uniform surface structures and elucidation of their reactivities.

6. CONCLUSIONS

When supported catalysts are made to be uniform and simple, essentially molecular, accurate determination of the catalytic structures is facilitated even in the working state, leading to structure−performance correlations that underlie catalyst designs. We have summarized how complementary techniques, including spectroscopy, atomic-resolution microscopy, and theory, can be used in concert for elucidation of the catalytic species, identification of reaction intermediates, and resolution of the roles of the metal, metal nuclearity, and the support and other ligands bonded to the metal in the activation of various reactants.

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Notes

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