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FINAL REPORT

ATOMICALLY DISPERSED SUPPORTED METAL CATALYSTS: UNDERSTANDING FUNDAMENTALS AND EXTENDING TO NEW CATALYST CLASSES

DE-FG02-04ER15513

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We have placed a major emphasis, as planned, on atomically dispersed supported metal catalysts. We wrote recent perspectives and reviews on this topic for *Trends in Chemistry, Chemical Reviews*, *Small*, and *Precision Chemistry*, which place the field in perspective and provide details in addition to those summarized here.

Samples with low loadings of metal on well-defined supports provide some of the best opportunities to determine metal–support structure and bonding. We illustrate methods for characterizing atomically dispersed heavy metals on metal oxide supports by aberration-corrected scanning transmission electron microscopy (STEM) complemented by fluorescence-detection extended X-ray absorption fine structure (EXAFS) and infrared spectroscopies. STEM images of Ir atoms derived from $Ir(C_2H_4)_2(acac)$ (acac = acetonato) on high-surface area MgO powder were obtained with minimized electron beam damage by quickly recording images near where focus had been established. The images show that iridium at a loading of 1.0 wt% on MgO calcined at 1073 K was atomically dispersed, populating much of the surface of the MgO particles, which had irregular shapes—consequently the iridium was bonded at various sites, to 2 or 3 surface O atoms. In contrast, MgO calcined at 1273 K consisted of almost perfectly cubic crystals, and Ir atoms at a loading of only 0.01 wt% on this nearly ideal support were anchored preferentially at edges and corners of (100) faces and bonded to 3 surface O atoms. The latter results indicate a path forward for determination of precise structures of atomically dispersed metals on crystalline metal oxide supports.

Supported catalysts that are important in technology prominently include atomically dispersed metals and metal clusters. When the metals are noble, they are typically unstable—susceptible to sintering—especially under reducing conditions. Embedding the metals in supports such as organic polymers, metal oxides, and zeolites confers stability on the metals, but at the cost of catalytic activity associated with the lack of accessibility of metal bonding sites to reactants. An approach to stabilizing noble metal catalysts while maintaining their accessibility involves anchoring them in molecular-scale nests that are in or on supports. The nests include zeolite pore mouths; zeolite surface cups (half-cages); raft-like islands of oxophilic metals bonded to metal oxide supports; clusters of non-noble metals (e.g., hosting noble metals as single-atom alloys); and nano-scale metal oxide islands that selectively bond to the catalytic metals, isolating them from the support. These examples illustrate a trend toward precision in synthesis of solid catalysts, and the latter two classes of nested catalysts offer realistic prospects for economical large-scale application.

Single-site $Ir(CO)_2$ complexes bonded to high-surface-area metal oxide supports, SiO_2, TiO_2, Fe_2O_3, CeO_2, MgO, and La_2O_3, were synthesized by chemisorption of $Ir(CO)_2(acac)$ (acac = acetylacetonate) followed by coating with each of the following ionic liquids (ILs): 1-*n*-butyl-3-methylimidazolium tetrafluoroborate, $[BMIM][BF_4]$, 1-*n*-butyl-3-methylimidazolium acetate, [BMIM][Ac], and 1-(3-cyanopropyl)-3-methylimidazolium dicyanamide, [CPMIM][DCA]. Extended X-ray absorption fine structure spectroscopy showed that site-isolated iridium was bonded to oxygen atoms of the support. Electron densities on the iridium enveloped by each IL sheath/support combination were characterized by carbonyl infrared spectroscopy of the iridium *gem*-dicarbonyls and by X-ray absorption near-edge structure data. The electron-donor/acceptor tendencies of both the support and IL determine the activity and selectivity of the catalysts for the hydrogenation of 1,3-butadiene, with electron-rich iridium being selective for partial hydrogenation. The results resolve the effects of the IL and support as ligands; for example, the effect of the IL becomes dominant when the support has a weak electron-donor character. The

combined effects of supports and ILs as ligands offer broad opportunities for tuning catalytic properties of supported metal catalysts.

Atomically dispersed iridium complexes were anchored on a reduced graphene aerogel (rGA) by the reaction of $Ir(CO)_2(acac)$ with oxygen-containing groups on the rGA. Characterization by X-ray absorption, infrared, and X-ray photoelectron spectroscopies and atomic resolution aberration-corrected scanning transmission electron microscopy demonstrates atomically dispersed iridium, at the remarkably high loading of 14.8 wt %. The rGA support offers sites for metal bonding comparable to those of metal oxides, but with the advantages of high density and a relatively high degree of uniformity, as indicated by the same turnover frequencies for catalytic hydrogenation of ethylene at low and high iridium loadings. The atomic dispersion at a high metal loading—and the high density of catalytic sites per unit of reactor volume, a key criterion for practical catalysts—set this catalyst apart from those reported.

The metal complex ($Zr(CH_3)_4(THF)_2$) was synthesized, characterized, and grafted onto partially dehydroxylated silica to give two surface species [(≡Si–O–)$Zr(CH_3)_3(THF)_2$] (minor) and [(≡Si–O–)$_2Zr(CH_3)_2(THF)_2$] (major), which have been characterized by solid-state NMR spectroscopy, IR spectroscopy, and elemental analysis. These supported pre-catalysts exhibit the best conversion of CO_2 to cyclic carbonates, as compared to the previously reported catalysts made by surface organometallic chemistry. We also worked on a number of other silica-supported complexes, including those of tungsten.

We worked on fundamental understanding of the interconversion of well-defined metal complexes and well-defined metal clusters in stabilizing environments, including zeolite cages and ligand envelopes. For example, rhodium *gem*-dicarbonyl complexes, $Rh(CO)_2$, bonded within the pore structure of zeolite HY and formed by the reaction of $Rh(CO)_2(acac)$ (acac = acetylacetonato) with OH groups on the zeolite surface were converted in >95% yield to $Rh_4(CO)_{12}$ by reaction with CO + water at 308 K, and the process was reversed by treatment of the supported clusters in helium at 353 K. The chemistry of these reactions was characterized by IR and X-ray absorption spectra recorded during the changes and by density functional theory. The cluster formation is driven by the water gas shift half-reaction, leading to generation of CO_2 and zeolite surface protons, and the reverse reaction proceeds via the half-reaction that completes the cycle of the water gas shift reaction. Thus, the overall process is cyclic–catalytic. The yield in the synthesis of $Rh_4(CO)_{12}$ is the highest reported, and the high selectivity is facilitated by the confining environment for the clusters in the zeolite supercages and the low density of OH groups on the zeolite surface (the zeolite Si:Al atomic ratio was 30). The results provide insights into the first steps of sintering of atomically dispersed metals on supports.

$Rh(I)(CO)_2$ complexes anchored to zeolite HY were converted into $Rh_4(CO)_{12}$ in the zeolite supercages upon exposure to flowing CO + H_2O at 35 °C, and the chemistry and kinetics were characterized with infrared spectroscopy. $Rh_6(CO)_{16}$ formed along with $Rh_4(CO)_{12}$, but only in low yield, although it is more stable than $Rh_4(CO)_{12}$. The formation of $Rh_6(CO)_{16}$ was hindered by trapping of $Rh_4(CO)_{12}$ in the supercages and by the low rate of transport of the mononuclear rhodium species. However, exposure of the sample to wet helium at 80 °C caused the $Rh_4(CO)_{12}$ to fragment, generating anchored $Rh(I)(CO)_2$ and also $Rh_6(CO)_{16}$. IR spectra recorded under various conditions led to elucidation of the reaction network for cluster formation and breakup and a strategy of repetitive treatments that boosted the yield of $Rh_6(CO)_{16}$ to >90%. The reversible formation and breakup of the rhodium carbonyl clusters were facilitated by the half-reactions of the water gas shift reaction, with gas-phase products identified by mass spectrometry. The results show how understanding of the reactions within a zeolite allows control of the nuclearity of

encaged metal clusters, an important class of catalyst.

We investigated metal nanoparticles encapsulated in zeolites. Supported rhodium nanoparticles (NPs) are well-known for catalyzing methanation in CO_2 hydrogenation. Now we demonstrate that the selectivity in this process can be optimized for CO production by choice of molecular sieve crystals as supports. The NPs are enveloped within the crystals with controlled nanopore environments that allow tuning of the catalytic selectivity to minimize methanation and favor the reverse water–gas shift reaction. Pure silica MFI (S-1)-fixed rhodium NPs exhibited maximized CO selectivity at high CO_2 conversions, whereas aluminosilicate MFI zeolite-supported rhodium NPs displayed high methane selectivity under the equivalent conditions. Strong correlations were observed between the nanoporous environment and catalytic selectivity, indicating that S-1 minimizes hydrogen spillover and favors fast desorption of CO to limit deep hydrogenation. Materials in this class appear to offer appealing opportunities for tailoring selective supported catalysts for a variety of reactions.

The reaction pathways on supported catalysts can be also tuned by optimizing the structures enveloping the catalyst, including amorphous materials. Such a design is particularly desired for CO_2 hydrogenation, which is characterized by complex pathways and multiple products. We reported an investigation of supported cobalt, which is known for its hydrocarbon production and ability to turn into a selective catalyst for methanol synthesis in CO_2 hydrogenation which exhibits good activity and stability. The crucial technique is to use the silica, acting as a support and ligand, to modify the cobalt species via Co–O–SiO_n linkages, which favor the reactivity of spectroscopically identified *CH_3O intermediates, that more readily undergo hydrogenation to methanol than the C–O dissociation associated with hydrocarbon formation. Cobalt catalysts in this class offer appealing opportunities for optimizing selectivity in CO_2 hydrogenation and producing high-grade methanol. By identifying this function of silica, we provide support for rationally controlling these reaction pathways.

Atomically dispersed supported catalysts are drawing wide attention because they offer properties different from those of conventional catalysts, with maximally efficient use of the metals. However, the performance of single-site catalysts is often limited by the lack of neighboring metal centers to cooperate in catalysis. Thus, there is motivation to extend this class to catalysts incorporating isolated metal pairs. We report pairs of iridium atoms on MgO initially stabilized by support oxygen and cyclooctadiene ligands and activated by the removal of the latter. These catalysts are stable in a range of environments, including CO, H_2, and C_2H_4 + H_2 at 298–353 K and are more active than analogous single-site catalysts in ethylene hydrogenation and hydrogen–deuterium exchange because the neighboring metal centers facilitate hydrogen activation. Moreover, the pair-site catalysts retain activity even in the presence of CO, which poisons the single-site analogues. Supported metal pair-site catalysts open pathways toward understanding and applications of supported molecular catalysts.

Although essentially molecular noble metal species provide active sites and highly tunable platforms for the design of supported catalysts, the susceptibility of the metals to reduction and aggregation and the consequent loss of catalytic activity and selectivity limit opportunities for their application. We demonstrated a new construct to stabilize supported molecular noble-metal catalysts, taking advantage of sterically bulky ligands on the metal that serve as surrogate supports and isolate the active sites under conditions involving steady-state catalytic turnover in a reducing environment. A longstanding challenge in catalysis by noble metals has been to understand the origin of enhancements of rates of hydrogen transfer that result from bonding of oxygen near metal sites. We investigated structurally well-defined catalysts consisting of supported tetrairidium

carbonyl clusters with single-atom (apical iridium) catalytic sites for ethylene hydrogenation. Reaction of the clusters with ethylene and H_2 followed by O_2 led to the onset of catalytic activity as a terminal CO ligand at each apical Ir atom was removed and bridging dioxygen ligands replaced CO ligands at neighboring (basal-plane) sites. The presence of the dioxygen ligands caused a 6-fold increase in the catalytic reaction rate. The rate enhancement is explained by the electron-withdrawing capability induced by the bridging dioxygen ligands, consistent with the inference that reductive elimination is rate determining. Electronic structure calculations demonstrate an additional role of the dioxygen ligands, changing the mechanism of hydrogen transfer from that involving equatorial hydride ligands to that involving bridging hydride ligands. This mechanism is made evident by an inverse kinetic isotope effect observed in ethylene hydrogenation reactions with H_2 and, alternatively, with D_2 on the cluster incorporating the dioxygen ligands, and is a consequence of quasi-equilibrated hydrogen transfer in this catalyst. The same mechanism accounts for rate enhancements induced by the bridging dioxygen ligands for the catalytic reaction of H_2 with D_2 to give HD. We posit that the mechanism involving bridging hydride ligands facilitated by oxygen ligands remote from the catalytic site may have some generality in catalysis by oxide-supported noble metals.

Atomically dispersed supported metal catalysts offer new properties and the benefits of maximized metal accessibility and utilization. The characterization of these materials, however, remains challenging. Using atomically dispersed platinum supported on crystalline MgO (chosen for its well-defined bonding sites) as a prototypical example, we demonstrate how systematic density functional theory calculations for assessing all the potentially stable platinum sites, combined with automated analysis of EXAFS spectra, leads to unbiased identification of isolated, surface-enveloped platinum cations as the catalytic species for CO oxidation. The catalyst has been characterized by atomic-resolution imaging and EXAFS and high-energy resolution fluorescence detection X-ray absorption near edge spectroscopy. The proposed platinum sites are in agreement with experiment. This theory-guided workflow (developed by coauthors Kulkarni and Bare) leads to rigorously determined structural models and provides a more detailed picture of the structure of the catalytically active site than what is currently possible with conventional EXAFS analyses. As this approach is efficient and agnostic to the metal, support, and catalytic reaction, we posit that it will be of broad interest to the materials characterization and catalysis communities.

Atomically dispersed metals on metal oxide supports are a rapidly growing class of catalysts. Developing an understanding of where and how the metals are bonded to the supports is challenging because support surfaces are heterogeneous, and most reports lack a detailed consideration of these points. Herein, we report two atomically dispersed CO oxidation catalysts having markedly different metal–support interactions: platinum in the first layer of crystalline MgO powder and platinum in the second layer of this support. Structural models have been determined on the basis of data and computations, including those determined by EXAFS and XANES, IR spectroscopy of adsorbed CO, and STEM. The data demonstrate the transformation of surface to subsurface platinum as the temperature of sample calcination increased. Catalyst performance data demonstrate the lower activity but greater stability of the subsurface platinum than of the surface platinum.

Atomically dispersed metal catalysts offer the advantages of efficient metal utilization and high selectivities for reactions of technological importance. Such catalysts have been suggested to be strong candidates for dry reforming of methane (DRM), offering prospects of high selectivity for synthesis gas without coke formation, which requires ensembles of metal sites and is a primary challenge in DRM catalysis. However, investigations of the structures of isolated metal sites on

metal oxide supports under methane reforming conditions are lacking, and the nature of the catalytically active sites is unknown. We report data characterizing the DRM reaction-driven structural evolution of a cerium oxide-supported catalyst, initially incorporating atomically dispersed platinum and the corresponding changes in catalyst performance. X-ray absorption and infrared spectra show that the reduction and agglomeration of isolated cationic platinum atoms to form small platinum clusters/nanoparticles is necessary for DRM activity. DFT calculations of the energy barriers for methane dissociation on atomically dispersed platinum and on platinum clusters support these observations. The results emphasize the need for *in-operando* experiments to assess the active sites in such catalysts. The inferences about the catalytically active species are suggested to pertain generally to a broad class of catalytic conversions involving the rate-limiting dissociation of light alkanes.

Supported atomically dispersed noble metal complexes and clusters provide high atom efficiency and size-dependent catalytic properties, but their stabilization remains a major challenge. We investigated atomically dispersed platinum and platinum clusters consisting of 7–14 atoms stabilized on CeO_x nanoislands on a porous silica support. The clusters were formed by reduction of the platinum single atoms in H_2 at 400 °C. The complexes were stable catalysts under high-temperature CO oxidation conditions. Redox cycles led to cluster formation from the atomically dispersed platinum and breakup at hundreds of °C, with the platinum remaining confined in the respective islands. The catalyst in each form at low temperatures (< 70 °C) was stable for ethylene hydrogenation in a flow reactor. The clusters are characterized by a turnover frequency 70-fold greater than that characterizing the single atoms. Computational results indicate a homolytic H_2 dissociation and moderately strong ethylene adsorption on the $Pt_{7–14}$ clusters, enhancing the catalytic activity by providing lower barriers than on platinum single atoms or the smallest platinum clusters (e.g., Pt_3).

Atomically dispersed cerium catalysts on an inert, crystalline MgO powder support were prepared by using both Ce(III) and Ce(IV) precursors. The materials were used as catalysts for CO oxidation in a once-through flow reactor and characterized by atomic-resolution STEM, XANES, X-ray photoelectron spectroscopy, and temperature-programmed reduction, among other techniques, before and after catalysis. The most active catalysts, formed from the precursor incorporating Ce(III), displayed a performance similar to that reported for bulk ceria under comparable conditions. The catalyst provided stable time-on-stream performance for as long as it was kept on stream, two days, increasing slightly in activity as the atomically dispersed cerium ions were transformed into ceria nanodomains represented as CeO_x and having increased reducibility on the MgO support. The results suggest how highly dispersed supported ceria catalysts with low cerium loadings can be prepared and may pave the way to improved efficiencies of cerium utilization in oxidation catalysis.

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