V.N.16 Platinum-Group Metal (PGM) Substituted Complex Oxide Catalysts

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Objectives

The increasing costs of platinum group metals (PGMs), arising from their scarcity, and from their ever-growing use in catalytic converters provides the imperative for research into better use of PGMs in catalysis. PGMs are extensively implicated in hydrogen generation from (hydro)carbon feedstocks, in the conversion of hydrogen into electricity in fuel cells, and in counter electrodes for photocatalytic water splitting. Other drivers for PGM abatement are the potential environmental impact of dispersed PGM particles, wastefully ablated from catalytic converters, and the complex geopolitics of sourcing these metals. A significant body of work, including from Santa Barbara, has pointed to the effectiveness of complex transition metal oxides substituted with small amounts of noble metal ions (notably, Pd^{2+}) in oxidation catalysis. This area of research has yielded a number of important surprises, chief amongst which is the increasing body of evidence pointing to Pd^{2+} in the oxide lattice, rather than Pd nanoparticles on the surface of the oxide, that are the active sites for CO oxidation. This has led us to question the paradigm of oxide-supported PGM nanoparticle catalysis – at least for a large class of important oxidation and partial oxidation reactions – and to envisage the development of catalysts that obviate problems inherent to supported catalysts; inefficiencies due to only surface atoms being accessible, particle sintering with concurrent loss of active surface area, and ablation. The materials focus is on complex oxides; complex implying they possess at least two crystallographically distinct cation sites. It has been clear

to us that a perovskite like $BaCeO_3$, which we have explored in some detail, behaves very differently from simple oxide supports like Al_2O_3. The objectives include exploring the catalytic role/activity of PGM ions such as Pd^{2+}, Pt^{2+}, and Au^{3+} substituted in complex oxide hosts. The target reactions are H_2, CO and hydrocarbon transformations, although the widespread use of PGM-based materials in many areas of catalysis means that the work will likely impact other areas of chemical conversion and energy as well. Our principal theme is the design of complex, multi-cation oxide hosts containing low quantities of substituted PGM ions, and their use as sinter- and poison-resistant replacements for conventional oxide-supported PGM catalysts.

Technical Barriers

The chief technical barrier to carrying out the work as described has been in learning how to prepare and stabilize the different oxides with either small PGM substitution, or that are stoichiometric in PGM-content. In general, PGM ions are oxophobic, which means that they do not easily form stable oxides, and the stability of the oxide decreases at increasing temperature. On the other hand, they are rather sluggish to react, which usually requires preparation at high temperatures, under conditions that push the limits of their stability. The second technical barrier is that many catalytic reactions take place under conditions wherein the PGM ion can be reduced to zerovalent (metal) nanoparticles. It is then important to distinguish reactions that are actually catalyzed by the PGM ion, rather than by the PGM nanoparticle.

Abstract

Substituted metal oxides containing ionic platinum group metal species have been attracting a great deal of attention because of their potential to reduce the amount of precious metals used in heterogeneous catalysis. To address questions surrounding catalytic activity of precious metal ions, we have continued to probe both well-defined model systems as well as lightly substituted simple and complex oxides. We continue to use CO oxidation as a test reaction, but in addition, we are employing a host of new, and industrially relevant reactions such as C–H bond activation, hydrocarbon combustion, and catalytic hydrogenation/dehydrogenation. We have used our understanding of experiments on known model compounds, in conjunction with detailed density functional electronic structure calculations, to determine potentially new catalytic systems based on markers of catalytic activity such as the d band position. In this past year, we have investigated Pd-substituted CeO_2. This substituted simple oxide has been well-studied for use in CO oxidation, NO_x reduction, and the water-gas shift reaction. We have investigated this compound, prepared by

ultrasonic spray pyrolysis, for partial oxidation and dry-reforming of CH_4. We have also, in this period, completed a comprehensive study of the electronic structure of gold compounds, in the search for new catalytic materials where the active element is gold. In this light, and as a precursor to further experiments, we have also examined the chemistry of Ir^{4+}. A survey of some of the progress is reported here.

Progress Report

4.1 $Ce_{1-x}Pd_xO_{2-\delta}$: Substituted ion *versus* supported metal

Pd-substituted CeO_2, $Ce_{1-x}Pd_xO_{2-\delta}$ was prepared as a high surface area powder using ultrasonic spray pyrolysis (USP). USP has been previously used for preparing mesoporous carbon materials; we have further developed this method to be applicable for substituted metal oxides. Metal nitrate precursors are mixed in a suitable molar ratio in water. The precursor solution is then nebulized into a fine mist and carried through a tube furnace at adjustable temperature, and the products are collected in water bubblers. The catalysts were extensively characterized using synchrotron X-ray diffraction and other techniques, confirming phase pure samples up to 10 mol% Pd substitution. $Ce_{0.95}Pd_{0.05}O_{2-\delta}$ was found to be active for the partial oxidation of CH_4 above 450^oC. Partial oxidation of CH_4 over $Ce_{0.95}Pd_{0.05}O_{2-\delta}$ yields the expected combustion products along with non-stoichiometric synthesis gas in the form of excess hydrogen gas. The excess hydrogen is a result of several secondary reactions occurring after combustion, including dry reforming of CH_4, steam reforming of CH_4, and water gas shift. We found that this material becomes catalytically active for C–H bond activation only after the Pd^{2+} ions have been reduced to Pd metal supported on CeO_2. This observation was confirmed from post-reaction analyses including X-ray diffraction, X-ray photoelectron spectroscopy, and by verifying the activity of the reduced Pd^0/CeO_2 catalysts for ethylene hydrogenation, a reaction that is known to require Pd^0. We have identified USP as a facile method for the preparation of substituted metal oxides, and also for the preparation of well-dispersed metal nanoparticles on oxide supports via reduction of substituted materials. Ongoing efforts are focused on the preparation of complex oxides by USP, including Pd-substituted perovskites, and solid acids.

4.2 Studies of gold compounds – Why are nanoparticles special?

As a strategy for addressing questions surrounding the possible catalytic role of ionic gold and platinum group species, we have looked to well-defined model compounds, and reported a comparison of two highly stable oxides containing square planar and isoelectronic Au^{3+} and Pd^{2+}: La_4LiAuO_8 and La_2BaPdO_5. Given that Pd^{2+} and Pt^{2+} in the solid state are well known to catalyze a variety of reactions, a natural question is whether Au^{3+}can behave similarly. We

determined that La_4LiAuO_8 is a very poor catalyst for the oxidation of CO to CO_2, in contrast to La_2BaPdO_5, which is quite a good catalyst for this reaction, despite being tested as a low surface area bulk powder. Electronic structure calculations revealed distinct differences in the average energy of the Pd 4d and Au 5d states – the Au d-states are held deep below the Fermi energy with the centroid positioned at approximately –5.0 eV. The Pd d-states of La_2BaPdO_5, on the other hand, are only about 2.5 eV below E_F. In the context of the Hammer–Nørskov d-band model, the distinct behaviors of these isoelectronic model compounds can be interpreted in terms of the differing abilities to interact with adsorbates: the d-states of La_4LiAuO_8 are not accessible, while the d-states of La_2BaPdO_5 are. Thus, we were led to the question: If the d-states of cationic $Au^{3+}$are too stabilized to be of interest for catalysis, where are the d-states located in compounds containing formally or partially anionic gold? Although a number of compounds of Au^- are known, none of them are sufficiently stable to warrant catalytic testing and many are air-sensitive; for example, dealloying of alkali-Au films exposed to O_2 has been found to occur near room temperature. $Au^{\delta-}$ species, however, which are encountered in polar intermetallics of Au with the early transition metals, are comparatively quite stable. As we began to study ordered gold alloys, however, similarities in the electronic structure of gold compounds containing Au in vastly different formal oxidation states quickly became apparent. It became clear that the formal oxidation state of Au was uninformative about the electronic structural features that dictate catalytic activity, namely, the energy of the Au d-states.

Using first principles bulk electronic structure calculations on a variety of Au compounds and species, encompassing a wide spectrum of formal oxidation states, coordination geometries, and chemical environments, we found that the center of the d band is linearly dependent on the degree of d-band filling. This is a general relationship for Au irrespective of its surroundings. Although changes in the d-band filling are small, the population of the d shell has a significant effect on the energy of the Au d-states. The ready formation of Au^- in compounds such as CsAu arises from Au possessing relatively stabilized s states, which also manifests as a relatively large Pauling electronegativity (for a metal) of 2.54. However, the destabilization of d-states results in Au readily forming compounds in the formal 3+ oxidation state (exemplified by La_4LiAuO_8). This schizophrenic behavior – summarized as s-electronegative but d-electropositive – is what results in the intermetallic compounds displaying such a wide variation in the Au d-band center position, and indeed, sharing the same range of d-band center positions as compounds of Au that are formally 3+.

4.3 Relativistic effects in the stability of Ir^{4+}

Relativistic effects lower the energy of (stabilize) the 6s orbital for an Ir atom, which is the result of contraction of

the s wavefunction towards the nucleus. Unlike the 6s state, the energy of the 5d orbitals increases and the wavefunction is shifted outward by the repulsion of the contracted s orbital. Both the wavefunction and energy of the s orbital are almost identical at the full-relativistic (FR) and scalar-relativistic (SR) levels. For the d orbitals, there are two channels in the FR approach. The SR energies and wavefunctions are located at the middle of the two FR channels, indicating that the SR state represents the average of the FR states. A similar trend is also found for Rh, but to a significantly lesser extent. This is a general trend for the 4d and 5d transition metals and has been noted in discussions of relativistic effects for molecules and clusters containing 4d and 5d transition metal atoms. However, the manner in which this leads to higher oxidation states in extended crystalline oxides had not previously been examined within a completely *ab-initio* framework. The valence and conduction states around the Fermi levels consist of Ir 6d and O 2p orbitals. For non-relativistic (NR) and SR cases, the spin degrees of freedom do not mix with the orbital degrees of freedom and the d orbitals can split into two groupings of states with t_{2g} and e_g symmetries arising from the octahedral crystal field. There is a greater extent of mixing between the Ir-d and O-p orbitals in IrO_2, suggesting a greater degree of covalency. Ir_2O_3 is a semiconductor, with fully occupied t_{2g} states. The SR pDOS have similar features to the NR pDOS, but the widths are increased in the SR pDOS and the Fermi levels are shifted upward, which is caused by the destabilization of the Ir 5d levels and associated increase in the energy difference between the Ir 5d and O 2p energy levels. For this reason, there is a larger contribution of Ir 5d character near the Fermi level in the SR DOS than in the NR DOS. The significant destabilization of the Ir 5d energy is the origin of the categorical stability of the Ir^{4+} state.

Future Directions

Currently, we are exploring the ultrasonic spray pyrolysis and microwave preparative routes for the preparation of a number of substituted complex oxides with Pd^{2+} and Pt^{2+}/Pt^{4+}. One such example is $LaFeO_3$, the Pd- substituted variant of which seems to be catalytically active even at room temperature. We are also planning to make model compounds such as La_2BaPdO_5 with higher surface area using USP. Another strategy for new complex oxides being explored is the concurrent development of solid acidity and Pd^{2+} substitution for reactions relevant to C–H activation. A third direction that has proved very fruitful in the past six months, is the use of microwave-assisted preparative methods which are yielding significant reductions (from days to minutes) in the preparation time of the more sluggish PGM oxides.

Publication list (including patents) acknowledging the DOE grant or contract:

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