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Project summary

Characterization of the Metal-Support Interface in Supported Metal and Supported Metal Complex Catalysts

Bruce C. Gates
Center for Catalytic Science and Technology
Dept. of Chemical Engineering
University of Delaware
Newark, DE 19716

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The extended X-ray absorption fine structure (EXAFS) technique has provided the first quantitative

characterizations of metal-support interface structures in highly dispersed supported metal catalysts. Thorough data have been obtained for Rh supported on γ -Al₂O₃ and on TiO₂. The EXAFS results for a number of metals on metal oxide supports show metal-oxygen interactions characterized by both short (2.0-2.2 Å) and long (2.5-2.8 Å) distances. The structural implications of these distances are still debated.

The objective of the present research is to gain fundamental understanding of the chemistry of metal-metal oxide interfaces by investigating structurally simple and well-defined supported metal catalysts. The characterizations take advantage of the unique capabilities of EXAFS spectroscopy; this technique is used in concert with infrared spectroscopy, temperature-programmed decomposition, and other methods. The strategy is to use organometallic precursors to prepare supported metal complexes with single metal atoms (mononuclear metal complexes) and extremely small supported metal clusters with nearly uniform nuclearities (numbers of metal atoms). Supported metal complexes and small, uniform supported metal clusters offer unprecedented opportunities for precise characterization of the metal structures by EXAFS spectroscopy; the smaller the metal cluster, the larger the fraction of the EXAFS signal that arises from the metal-support interface and the greater the opportunity for accurate characterization of the interface structure.

[HRe(CO)₅], [H₃Re₃(CO)₁₂], [Ir(CO)₂(acac)], and [Ir₄(CO)₁₂], among others, were chosen to be the precursors. Partially hydroxylated MgO, La₂O₃, zeolite NaX, and zeolite KL, among others, were chosen to be the supports, as the chemistry of the metal carbonyls on the basic surfaces of these supports is relatively well understood, being similar to that occurring in basic solutions and allowing synthesis in high yields of supported metal carbonyls including Re(CO)₃{OMg}₂{HOMg} (where the braces denote groups terminating MgO), [HIr₄(CO)₁₁]⁻, and [Ir₆(CO)₁₅]²⁻, among others, on the surfaces. One of the goals was to form and decarbonylate the metal cluster anions on the supports without changing their nuclearities (numbers of metal atoms).

The MgO support is the one of primary interest, because it offers several advantages for characterization of the samples by X-ray absorption spectroscopy. In contrast to the structurally more complex γ -Al₂O₃ and TiO₂, MgO (which has the rock salt structure) exhibits predominantly (100) faces, even in the powder form. Thus the surface of

MgO is relatively simple and well defined and a good choice for characterization of the metal-support interface. Furthermore, as both the O^{2-} and Mg^{2+} ions are present in the same surface layers, both the Ir-O and Ir-Mg interactions are expected to be well characterized by the EXAFS (extended X-ray absorption fine structure) data. EXAFS evidence of interactions between supported metals and cations of the support has been reported only rarely.

The results of this research provide a precise characterization of the metal-support interface. The EXAFS data reduction has been carried out with an improved method, including statistical analysis; the structural parameters are beginning to be reported for the first time with confidence limits determined on the basis of estimates of the noise in the data.

D. Importance of the problem

Extensive research has been done in the preceding decade in attempts to understand the nature of the metal-support interface and to interpret the effects of supports on the performance of supported metal catalysts. This work has demonstrated the role of reducible metal oxide supports (e.g., MnO_2) in forming overlayers (e.g., of TiO_x) that partially cover the metal and may act as catalyst promoters, but the work has fallen short of providing insights into the interactions between metals and typical (nonreducible) metal oxide supports. The significance of the research summarized here is that it takes advantage of (1) new synthesis procedures for the preparation of structurally simple and nearly uniform samples and (2) powerful new physical characterization methods (especially, EXAFS spectroscopy) to determine the structures of supported metal species, including the structure of the metal-support interface. For the first time, metal-oxygen bonds have been identified and the coordination of the metal characterized quantitatively. Thus, this work is unique in placing the issues of the metal-support interactions on a quantitative foundation of structural chemistry.

6. Project Output

A. Major recent accomplishments

Rhenium subcarbonyls on MgO

Structures formed on the surface of almost fully dehydroxylated MgO by adsorption of $[HRe(CO)_3]$ were

characterized by EXAFS spectroscopy. The rhenium carbonyl initially was molecularly adsorbed, interacting with the MgO surface as the proton was partially removed by a basic oxygen of the surface; the average Re-C and Re-O* coordination numbers (where O* refers to the carbonyl oxygen) are about 5. There is no EXAFS evidence for interactions of carbonyl oxygen with the surface. The average Re-C and Re-O* distances are 1.94 and 3.13 Å, respectively. When adsorbed $[\text{HRe}(\text{CO})_5]$ was heated to 80°C in H_2 , it lost two CO ligands per Re and formed a subcarbonyl formulated as $[\text{Re}(\text{CO})_3(\text{HO-Mg})_2(\text{O-Mg})]$. The average Re-C, Re-O*, and Re-O distances are 1.91, 3.12, and 2.13 Å, respectively. The Re-O distance is equal, within ± 0.1 Å, to the metal-oxygen distances in the only other well-characterized metal subcarbonyls on metal oxides and to the metal-oxygen distances in numerous organometallic complexes with oxygen-containing ligands.

$[\text{HRe}(\text{CO})_5]$ also reacted with the surfaces of partially dehydroxylated (about 55%) MgO powder. The initial surface species were again molecularly adsorbed $[\text{HRe}(\text{CO})_5]$, which, upon heating to 80°C in H_2 or under vacuum, gave rhenium subcarbonyls with three CO ligands and three oxygen-containing ligands provided by the MgO surface. Infrared spectra indicate C_{3v} symmetry in both structures, with bands at 2011(vs), 1895(vs), and 1862 (sh) cm^{-1} for rhenium subcarbonyl on the partially dehydroxylated MgO and at 2017(vs), 1908(vs), and 1867(sh) cm^{-1} for the rhenium subcarbonyl on the nearly dehydroxylated MgO. The average bond distances were determined by EXAFS: On the partially dehydroxylated MgO, the Re-C, Re-O*, and Re-O_s (O_s is a surface oxygen) bond lengths were 1.87, 3.11; and 2.13 Å, respectively; and on the nearly dehydroxylated MgO, they are as stated above. These distances indicate greater electronic donation (backbonding) from the Re to the CO on the partially hydroxylated MgO than from the Re to the CO on the almost fully dehydroxylated MgO surface, suggesting electron transfer from the MgO to the Re. The MgO surface is thus modelled as a rigid multidentate electron donor analogous to a molecular ligand. The X-ray absorption near edge data confirm a higher electron density on the Re atoms bonded to the oxygens of partially dehydroxylated MgO than on Re atoms bonded to almost fully dehydroxylated MgO.

Rhenium subcarbonyls on MgO powder were also prepared by adsorption and decomposition of $[\text{Re}_2(\text{CO})_{10}]$ and characterized by infrared spectroscopy. The MgO was treated at various temperatures to give surfaces ranging from those that were virtually fully dehydroxylated to those that were highly hydroxylated; methoxylated surfaces were also prepared by treatment of the MgO with methanol. The rhenium

subcarbonyl on the surface has distinctive carbonyl infrared spectra very similar to those of molecular analogues that allow identification of the surface ligands bonded to the rhenium as O^{2-} on the highly dehydroxylated surface, OH^- on the hydroxylated surface, and CH_3O^- on the methoxylated surface. A family of surface species is identified, including $[Re(CO)_3\{O-Mg\}_3]$, $[Re(CO)_3\{HOMg\}_3]$, $[Re(CO)_3\{HO-Mg\}_2\{O-Mg\}]$, and $[Re(CO)_3\{CH_3O-Mg\}_3]$.

Iridium clusters on MgO: characterization of the metal-support interface

X-ray absorption spectroscopy was used to characterize the metal-support interface in catalysts consisting of very small Ir clusters of nearly uniform nuclearity on the surface of MgO powder. $[Ir_4(CO)_{12}]$ on MgO was converted in high yield into $[HIr_4(CO)_{11}]^-$ and separately into $[Ir_6(CO)_{15}]^{2-}$. EXAFS data are consistent with the hypothesis that each cluster retained its nuclearity upon decarbonylation. The average Ir-Ir coordination in Ir_4/MgO is 2.6 neighbors at a distance of 2.72 Å, and the structure is modeled as a mixture of tetrahedra and four-atom rafts on MgO. Another sample was treated in H_2 at 350°C to give a typical supported metal catalyst having a distribution of Ir clusters averaging 10 Å in diameter. The Ir-support interfaces in Ir_4/MgO and Ir_6/MgO are characterized by single Ir-Mg coordinations at 1.6 Å and fourfold Ir-O coordinations at 2.6 Å; the interface Ir atoms are suggested to be atop Mg ions in the (100) faces of MgO.

Characterization of the metal-support interface in supported metal complexes and metal clusters: implications for catalysis

X-ray absorption spectra characterizing the metal-support interface in supported metal complexes and supported metal catalysts have been summarized and evaluated. Transition metal complexes on nonreducible metal oxide supports are bonded with metal-oxygen distances of approximately 2.15 Å; the bonding distance is only weakly sensitive to the oxidation state of the metal. Nearly this same metal-oxygen distance is characteristic of the metal-support interface in metal-oxide-supported metal clusters following reduction in H_2 at high temperatures (HTR: $T > 450^\circ C$). The metals at the interface may be polarized sufficiently that they bond with the underlying oxygen much as the metals in mononuclear metal complexes bond with it.

When the supported metals are treated in H_2 at low temperatures (LTR: $T < 350^\circ C$) or prepared under He with partially hydroxylated supports, another metal-support oxygen distance is observed, typically 2.5-2.7 Å. This distance is suggested to characterize the metal-oxygen interaction in fully reduced (zerovalent) supported metals. The differences in catalytic performance of low-temperature-reduced (LTR) and high-temperature-reduced (HTR) supported metals are probably related to the differences in electronic properties of the supported metal clusters resulting from the different pretreatment conditions in H_2 . These differences are inferred to be associated with the above-mentioned types of metal-support interactions.

B. Five Recent Publications based on this work

1. J.-R. Chang, L. U. Gron, A. Honji, K. M. Sanchez, and B. C. Gates, "Mononuclear Rhenium Carbonyls on MgO : Characterization of the Metal-Support Interface by Extended X-Ray Absorption Fine Structure Spectroscopy," *J. Phys. Chem.*, 1991, 95, 9944.
2. C. J. Papile and B. C. Gates, "Rhenium Subcarbonyls on Magnesium Oxide: Identification of the Surface Oxo and Hydroxo Ligands by Infrared Spectroscopy," *Langmuir*, 1992, 8, 74.
3. A. Honji, L. U. Gron, J.-R. Chang, and B. C. Gates, "Ligand Effects in Supported Metal Carbonyls: X-Ray Absorption spectroscopy of Rhenium Subcarbonyls on Magnesium Oxide," submitted to *Langmuir*.
4. D. C. Koningsberger and B. C. Gates, "Nature of the Metal-Support and Metal-Promoter Interface: Implications of X-Ray Absorption Spectroscopy for Catalysis, submitted to *Catal. Lett.*
5. B. C. Gates and D. C. Koningsberger, "Structures of Supported Metal Clusters," *CHEMTECH*, to be published, May, 1992.

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