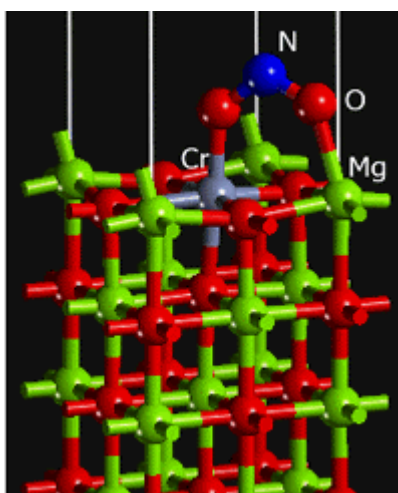




DeNO_x and DeSO_x activity of rare-earth, transition-metal and mixed-metal oxides: systematic design of better catalysts through orbital-band interaction studies

Researchers at the Brookhaven national Laboratory have used Accelrys' density functional code (DFT) CASTEP to carry out a detailed study of the interaction of various pollutant molecules on the surfaces of rare-earth, transition-metal, and mixed-metal oxides, and to investigate how these interactions change as a function of surface defects and doping with different metals.

Stringent federal and environmental regulations have placed a high priority on developing catalysts to prevent N-, S-, and C-containing pollutants from entering the earth's atmosphere. Accelrys' quantum physics code CASTEP has been used to carry out a detailed study of the interaction of various pollutant molecules on the surfaces of rare-earth, transition-metal, and mixed-metal oxides, and to investigate how these interactions change as a function of surface defects and doping with different metals. The insight gained from these studies, augmented with sophisticated spectroscopy techniques is providing invaluable guidance in the design of new metal-oxide-based catalysts.



Chemisorption of NO₂ on a Cr-doped MgO(100) surface. Electrons in Cr 3d levels above the MgO valence band lead to strong pollutant binding and facilitate N-O bond dissociation

Numerous industrial processes involve combustion or oxidation of chemicals and fuels that constantly produce harmful molecules like NO, NO₂, N₂O, SO₂, H₂S, CO *etc.* Besides being hazardous to human health through environmental pollution, these molecules cause millions of dollars worth of damage annually in the form of acid rain and building corrosion. One cannot overstate the importance of designing better catalysts to prevent these molecules from entering the earth's atmosphere.

Metal-oxides, as a general class of materials, have shown great promise in such applications. In fact, the surface chemistry of oxides is relevant to many technological applications: catalysis, photo-electrolysis, electron-device fabrication, corrosion prevention, and sensor development, to name a few. They possess a wide variety of structures and electronic properties. For instance, the rare-earth oxide MgO is strongly ionic, and a high-bandgap insulator, while the transition-state metal oxide TiO₂ possesses half the bandgap as MgO, and can best be described as an ionic-covalent material. Add to this scenario mixed-metal oxides like MgMoO₄, FeMoO₄ or NiMoO₄, and doped oxides like Cr_xMg_{1-x}O, and one has a rich variety of materials with metal-centers of different coordinations and environments. Recent experiments already demonstrate increased DeNO_x, DeSO_x and HDS activity of certain mixed-metal and doped-metal oxides. However, to optimize their catalytic performance it is necessary to possess an atomic/electronic-level understanding of the interaction of the pollutant molecules with the oxide surfaces.

Dr Jose Rodriguez of Brookhaven National Laboratory and his collaborators have used Accelrys' plane-wave density functional theory (DFT) code CASTEP to carry out detailed investigations of the interaction of the above pollutant molecules with the

surfaces of MgO [1-8], TiO₂[9, 10], Cr₂O₃ [5], ZnO [1], and CeO₂ [2]. Also studied were the electronic properties of mixed-metal oxides [11, 12], and pure and doped metal surfaces [13]. Much of the above work also investigated the effects of structural defects (steps, kinks, corners, O-vacancies) and doping with a second metal.

The Brookhaven group has also invested a significant experimental effort in order to characterize the atomic/ionic species and the electronic density of states on the oxide surfaces, using state-of-the-art spectroscopic techniques. Some of these include: X-ray absorption near-edge spectroscopy (XANES), X-ray and Ultraviolet photoemission spectroscopy (XPS, UPS), and thermal desorption mass spectroscopy (TDS).

The close coupling between theory and experiment is making possible a fundamental understanding of many phenomena associated with the chemistry of molecules on oxide surfaces. In particular, the importance of band-orbital interactions for the reactivity of oxide surfaces has become clear, and a correlation between the electronic and chemical properties of mixed and doped oxides has been established. This has opened the way for using simple models based on band-orbital mixing to provide a conceptual framework for modifying or controlling the chemical activity of pure oxides, and for better engineering of mixed-metal oxides.

References

1. "Adsorption and Decomposition of H₂S on MgO(100), NiMgO(100) and ZnO(0001) surfaces: A First-Principles Study," J. A. Rodriguez and A. Maiti, *J. Phys. Chem.* **104**, 3630 (2000).
2. "Chemistry of NO₂ on CeO₂ and MgO: Experimental and Theoretical Studies on the Formation of NO₃," J. A. Rodriguez, T. Jirsak, S. Sambasivan, D. Fischer, and A. Maiti, *J. Chem. Phys.* **112**, 9929 (2000).
3. "Interaction of SO₂ with MgO(100) and Cu/MgO(100): Decomposition Reactions and the Formation of SO₃ and SO₄," J. A. Rodriguez, T. Jirsak, A. Freitag, J. Z. Larese, and A. Maiti, *J. Chem. Phys. B* **104**, 7439 (2000).
4. "Interaction of NO and NO₂ with MgO(100): Photoemission and Density Functional Studies," J. A. Rodriguez, T. Jirsak, J. Z. Larese, and A. Maiti, *Chem. Phys. Lett.* **330**, 475 (2000).
5. "Studies on the Behavior of Mixed-Metal Oxides and Desulfurization: Reaction of H₂S and SO₂ with Cr₂O₃ (0001), MgO (100) and Cr_xMg_{1-x}O(100)," J.A. Rodriguez, T. Jirsak, M. Pérez, S. Chaturvedi, M. Kuhn, L. González, and A. Maiti, *J. Am. Chem. Soc.* **122**, 12362 (2000).
6. "Studies on the Behavior of Mixed-Metal Oxides: Adsorption of CO and NO on MgO(100), Ni_xMg_{1-x}O(100) and Cr_xMg_{1-x}O(100)," J.A. Rodriguez, T. Jirsak, M. Pérez, L. González, and A. Maiti, *J. Chem. Phys.* **114**, 4186 (2001).
7. "Coadsorption of Sodium and SO₂ on MgO(100): Alkali Promoted S-O Bond Cleavage," J. A. Rodriguez, M. Perez, T. Jirsak, L. Gonzalez, and A. Maiti, *Surf. Sci.* **477**, L279 (2001).
8. "DeNO_x Reactions on MgO(100), Zn_xMg_{1-x}O(100), Cr_xMg_{1-x}O(100) and Cr₂O₃ (0001): correlation between Electronic and Chemical Properties of Mixed-Metal Oxides," J. A. Rodriguez, M. Perez, T. Jirsak, L. Gonzalez, A. Maiti, and J. Z. Larese, *J. Phys. Chem. B* **105**, 5497 (2001).
9. "Interaction of Sulfur with TiO₂ (110): Photoemission and Density-Functional Studies," J. A. Rodriguez, J. Hrbek, J. Dvorak, T. Jirsak, and A. Maiti, *Chem. Phys. Lett.* **336**, 377 (2001).
10. "Chemistry of NO₂ on oxide surfaces: Formation of NO₃ on TiO₂(110) and NO₂:O vacancy interactions," J. A. Rodriguez, T. Jirsak, G. Liu, J. Dvorak, and A. Maiti, *J. Am. Chem. Soc.* **123**, 9597 (2001).
11. "Phase Transformations and Electronic Properties in Mixed-Metal Oxides: Experimental and Theoretical Studies on the Behavior of NiMoO₄ and MgMoO₄," J. A. Rodriguez, J. C. Hanson, S. Chaturvedi, A. Maiti, and J. L. Brito, *J. Chem. Phys.* **112**, 935 (2000).
12. "Studies on the behavior of mixed-metal oxides: Structural, Electronic and Chemical properties of β-FeMoO₄," J. A. Rodriguez, J. C. Hanson, S. Chaturvedi, A. Maiti, and J. L. Brito, *J. Phys. Chem. B* **104**, 8145 (2000).
13. "Interaction of Sulfur with Pt(111) and Sn/Pt(111): Effects of Coverage and Metal-Metal Bonding on Reactivity towards Sulfur," J. A. Rodriguez, J. Hrbek, M. Kuhn, T. Jirsak, S. Chaturvedi, and A. Maiti, *J. Chem. Phys.* **113**, 11284 (2000).

[Careers](#) | [Legal / Terms of Use](#) | [Contact us](#)