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1. Introduction:

By some accounts, catalysis impacts ≥ 30% of GDP in developed countries [Maxwell, I. E. *Nature* **394**, 325-326 (1998)]. Catalysis is the enabling technology for petroleum production, for control of gaseous emissions from petroleum combustion, and for the production of industrial and consumer chemicals. Future applications of catalysis are potentially even more far reaching. There is an ever-growing need to move the

economy from a fossil-fuel energy base to cleaner alternatives. Hydrogen-based combustion systems and fuel cells could play a dominant role, given a plentiful and inexpensive source of hydrogen. Photocatalysis is the most promising clean technology for hydrogen production, relying solely on water and sunlight, but performance enhancements in photocatalysis are needed to make this technology economically competitive.

Given the enormously wide spread utilization of catalysts, even incremental performance enhancements would have far-reaching benefits for multiple end-use sectors. In the area of fuel and chemical production, such improvements would translate into vast reductions in energy consumption. At the consumption end, improvements in the catalysts involved would yield tremendous reductions in pollution. In the area of photocatalysis, such efficiency improvements could finally render hydrogen an economically viable fuel.

Prerequisite to the non-empirical design and refinement of improved catalysts is the identification of the atomic-scale structure and properties of the catalytically active sites. This has become a major industrial research priority. *The focus of this research program was to combine atomic-resolution Z-contrast electron microscopy with first-principles density functional theory calculations to deliver an atomic-scale description of heterogeneous catalytic systems that could form the basis for non-empirical design of improved catalysts with greater energy efficiency.*

2. Technical results:

The Milestone Plan for this contract includes four major objectives. In targeting these objectives numerous inter-related science problems were addressed. What follows is a summary of the scientific products that resulted from targeting each objective. This report is comprehensive to the entire project. Progress during the first two years was also reviewed in the first two annual reports.

2.1 Objective 1) Analysis of catalyst thermal-stability enhancers.

2.1.1 Analysis of the mechanism by which a γ-alumina support loses surface area. Discovery of the atomic-scale details of the mechanism of conversion of γ- to θ-alumina. [Results reported in: 4,6]

One serious practical problem in the use of supported metal catalysts is that at elevated temperatures (1000–1100°C), high surface area catalytic support materials, such as γ–alumina, undergo a catastrophic loss of porosity through sintering. Stabilization of γ–alumina, therefore, represents an important industrial and commercial problem. To improve thermal stability, catalytic materials are doped with metal atoms. Through empirical testing it is known that La and Ba are most effective in stabilizing at elevated temperatures, while Sm and Ca are ineffective. Our objective was to analyze known thermal stability enhancers to reduce empiricism in the design of more durable catalytic materials. Early on in our investigations we realized that an understanding of the mechanisms of the polymorphic transformations is a necessary prerequisite to understanding how dopant atoms influence thermal stability. We therefore studied the phase transition of γ– to θ–alumina by first principles calculations. This is the critical first step in the sintering process that leads to loss of porosity.

Although the unit cell of cubic γ–alumina looks quite different from that of monoclinic θ–alumina, we found that both of them can be redefined to cells containing $Al_{16}O_{24}$ that are very similar. (See Fig. 1.) This provided us with a clear framework to study the transformation of γ– to θ–alumina. It is found that when some of the aluminum atoms in γ–alumina move to specific sites, a close approximation of θ–alumina is formed.
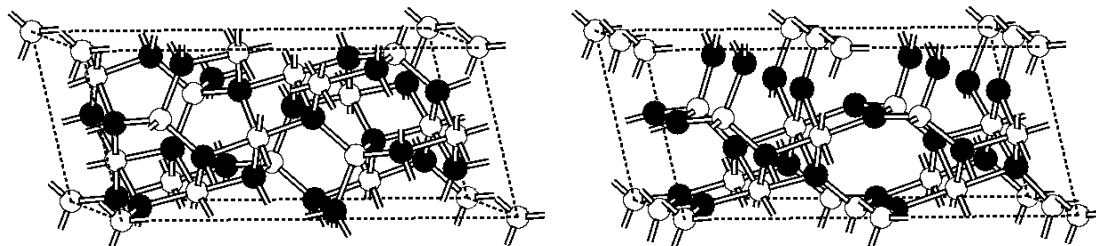
Figure 1. (left) Defect-free cell γ_N; (right) cell θ_N with translation of origin (solid spheres: oxygen, empty sphere: aluminum). Note the similarity, esp. in the oxygen sublattice.

We identified two possible reordering schemes that take γ-alumina and convert it to θ-alumina: scheme **A**, involves reordering eight aluminum atoms; scheme **B**, involves reordering fourteen aluminum atoms. In either case, the oxygen sublattice remains essentially unchanged. The θ-alumina models that result from these two different re-orderings are translationally equivalent and optimize to the experimentally determined structure within the margins of error of the models. The orientation relationship between γ– and θ–alumina defined by these models agrees with experimental observations.

Based on a comparison of the energy differences obtained from first principles calculations, the aluminum migration is found to take place first in the vicinity of cation vacancies to reduce strong Al–Al interactions. Scheme **B** is energetically less favorable. In addition, as six more Al atoms are reordered in scheme **B**, scheme **B** is also statistically less probable. Starting from a lowest energy configuration of γ–alumina, the lowest energy pathway of transformation by scheme **A** was mapped out. The computed conversion rate based on this pathway recovers the experimental transformation temperature to high accuracy. (See Fig. 2.)
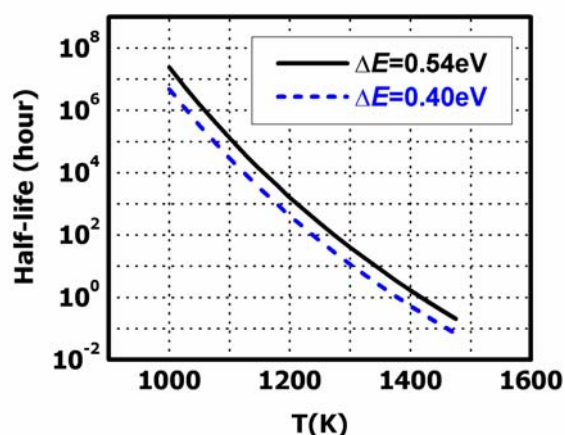
Figure 2. Half-life for γ-alumina $\rightarrow$ θ-alumina transformation as a function of temperature. The black curve is a preliminary calculation. The blue curve (0.4 eV barrier) is our best calculation, and is in excellent agreement with the observed transformation time of about 10 hours at 1300 K.

The experimentally observed translational and rotational interfaces in θ–alumina can be explained by different aluminum migration paths (resulting in models **A**, **B** and their variants) in neighboring domains during the γ– to θ–alumina transformation. It is anticipated that this detailed atomic-scale description of the phase transformation will provide the insight necessary for targeted doping and materials preparation to hinder the transformation process thereby leading to improved thermal stability and more durable heterogeneous catalysts.

2.1.2 Analysis of the mechanism by which doping of γ-alumina with La increases the thermal stability. [Results reported in: 8]

As mentioned in section 2.1.1, γ-alumina is one of many polytypes of aluminum oxide that is used extensively as a catalytic support (i.e., as a substrate on which catalyst metal particles are dispersed). A porous form of γ-alumina is used that has a large specific surface area. At temperatures in the range 1000-1200ºC, however, γ-alumina transforms rapidly into the thermodynamically stable α-alumina phase (corundum), the latter of which has low porosity and low surface and is therefore a poor catalytic support. Industrially, this problem is averted by doping γ-alumina with La. Many other dopants have been tried, but these are typically less effective at stabilizing the alumina, or can only be incorporated into the alumina only through more expensive processing. It is clear that an understanding of the mechanism by which La stabilizes the alumina is essential for the non-empirical design of more effective and more economical methods of stabilizing alumina than the current La doping technology. Toward this goal we carried out atomic-resolution Z-STEM and first-principles density functional theory studies of the La/γ-alumina system.

Combining our experimental and theoretical tools to investigate the role of La in stabilizing γ-alumina led to an unambiguous conclusion: La atoms coat the surfaces of alumina, dispersed as single atoms. A compelling demonstration is provided by the Z-STEM images of dispersed La atoms on a γ-alumina surface shown in Fig. 3. By changing the focus point of the microscope electron beam from the top surface to the middle of the sample to the bottom surface, the La-atom images are seen to gradually fade and finally reappear, confirming that the La atoms are in fact on the two surfaces. The image in Fig. 4 shows single La atoms superposed on the crystal lattice planes formed by the substrate. The image shows that two distinct positions for La surface atoms were identified. In addition, Our theoretical calculations found that La atoms favor the surfaces over bulk sites by substantial energy differences (~4 eV), with several configurations, including the two observed in Fig. 3 having comparable energies (Fig. 5 shows a schematic, showing that a La atom on a (100) surface induces a significant local reconstruction event). In addition, the theoretical calculations demonstrated that single La adatoms atoms have a much larger binding energy on γ-alumina (7.5-9 eV) than α-alumina (4-5 eV), which is the final product of the transformation of transition aluminas.

Taken together, the above results provide the following explanation of how doping of alumina with La inhibits sintering: La atoms coat the surfaces of porous alumina as dispersed single adatoms. As the temperature is increased, their presence on the surface prohibits sintering and transformation to non-porous α-alumina, because any sintering would either trap La atoms in the bulk, which is energetically unfavorable, or

expel them to the surface of α-alumina, which is again not favored energetically. La in fact delays the onset of the transformation by about 150 K. It is anticipated that this new understanding of the mechanism by which La stabilizes alumina as a catalytic support will lead to the identification of improved and/or less expensive thermal stability enhancers.
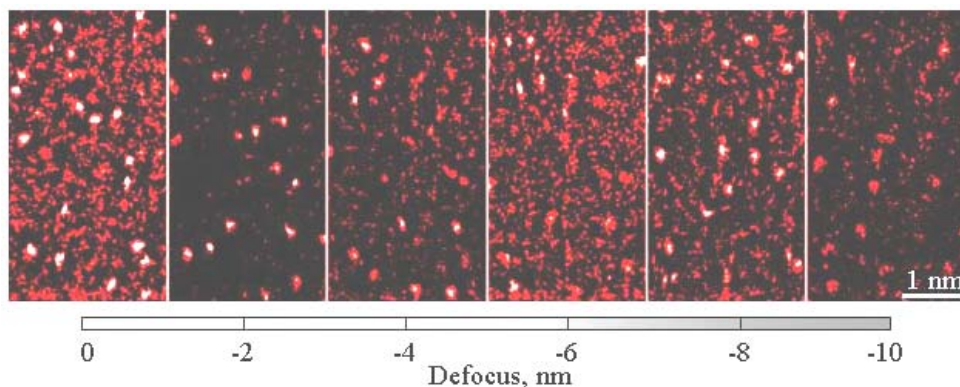
Figure 3. Z-contrast image of a La-doped γ-Al$_2$O$_3$ sample obtained by changing the focus of the beam from the top surface (ca. 0 nm) of the sample to the bottom surface (ca. 8 nm).
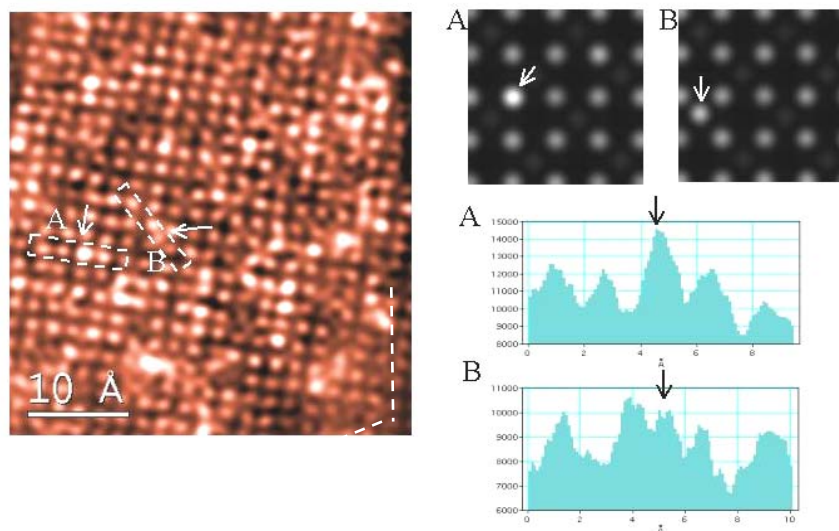
Figure 4. Z-contrast image of a La-doped γ-Al$_2$O$_3$ sample, showing the individual La atoms (the bright spots). The (100) surface of γ-Al$_2$O$_3$ is exposed. Two distinct positions (A and B) for La surface atoms are identified.
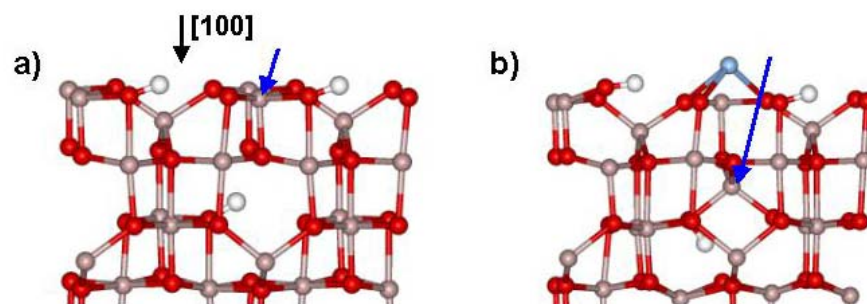
Figure 5. Schematics of the configurations for the (100) surface of γ-Al$_2$O$_3$, determined by first-principles calculations: (a) undoped, and (b) La-doped. The Al, O, H, and La atoms are shown in gray, red, white, and blue, respectively. When the La atoms is present on the surface, a surface Al atom relaxes from the surface into a cation vacancy as indicated by the blue arrow. The La atom occupies a site close to the initial location of the Al atom and binds to the nearest three oxygen atoms.

2.2 Objective 2) Analysis of catalytic surfaces

      2.2.1 Enhancements of the Z-STEM instrumentation. [Results reported in: 12]

      The main factor that limits the resolution of a Z-STEM instrument is spherical aberration (C$_s$) of the objective lens. This aberration is unavoidable in conventional electron lenses, and so in order to improve the performance of the instrument, the lens aberrations must be corrected. During the project period, both the 100 kV VG Microscopes HB501UX and the 300 kV HB603U STEM at Oak Ridge National Laboratory (ORNL) were fitted with aberration correctors constructed by Nion Co. This improved the resolution of the 100 kV instrument from 2.2 Å (full-width-half-maximum probe intensity) to around 1.3 Å (See Fig. 6.)

Figure 6. HAADF images of silicon viewed down the [110] direction. (a) Before correction, the individual atomic columns are not resolved. (b) After correction, the "dumbbells", separated by only 1.4 Å are clearly resolved.
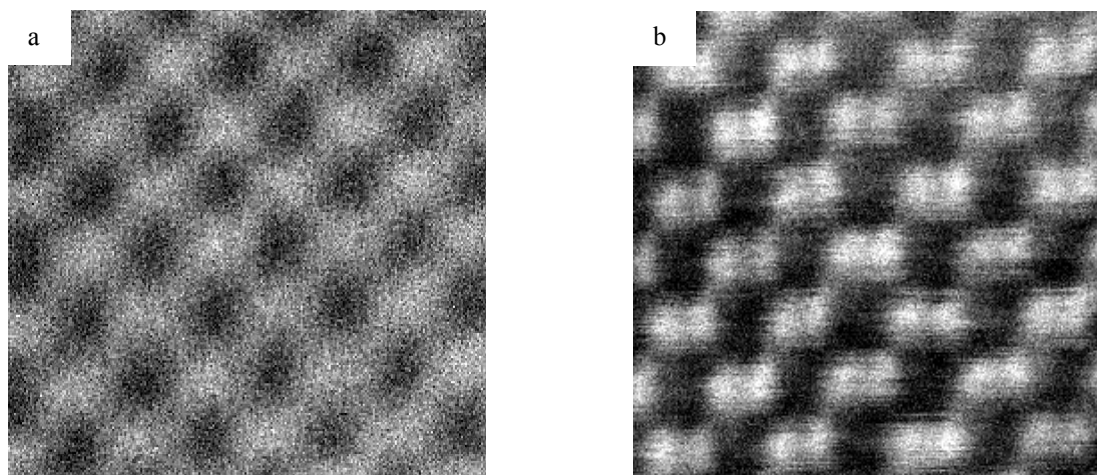
The 100 kV instrument is now very comparable in performance to the *uncorrected* 300 kV HB603U STEM which, before correction, also had a directly interpretable resolution of 1.3 Å. After installing an aberration corrector on the 300 kV STEM, the resolution improved from 1.3 Å to ca. 0.75 Å and the 300 kV instrument is now routinely resolving features at the sub-angstrom level.

Figure 7 compares the performance before and after fitting a Nion aberration-corrector to the ORNL 300 kV STEM. On the left is the Scherzer optimum probe profile for the uncorrected microscope, the Ronchigram, and an image and line trace from Si ⟨110⟩. The right hand side shows the 0.5 Å probe predicted after aberration-correction, showing the same current squeezed into a smaller, brighter probe. Such a probe should therefore give greatly improved contrast and signal to noise ratio from single atoms and crystals with spacings in the 1 – 2 Å range. Experimentally, the Ronchigram does show the anticipated 2.5-fold increase in the extent of flat phase, indicating that an instantaneous probe of 0.5 Å size has indeed been generated by the corrector. The resolution obtained in the image, however, is limited to around 0.9 Å due to instabilities.

Nevertheless, the Si ⟨110⟩ image now shows more contrast, with much deeper dips between the dumbbells. In addition, the effect of probe tails has been much reduced. We no longer see the weak subsidiary maxima in the center of the channels that are present in the uncorrected image.

BEFORE CORRECTION: 1.3 Å PROBE **AFTER CORRECTION: 0.5 Å PROBE**

Figure 7. Comparison of the performance of the 300 kV STEM before correction (left) and after installation of the aberration corrector (right). Panels show, from top to bottom, the theoretical probe profile, experimental Ronchigrams and images and intensity profiles of Si ⟨110⟩.

These features come from the extended tails on the uncorrected probe. When this probe is centered on a channel, the tail overlaps the nearest six columns of Si giving a weak secondary peak.

After correction the tails are reduced in intensity and brought closer to the central peak so this spurious feature is no longer present.
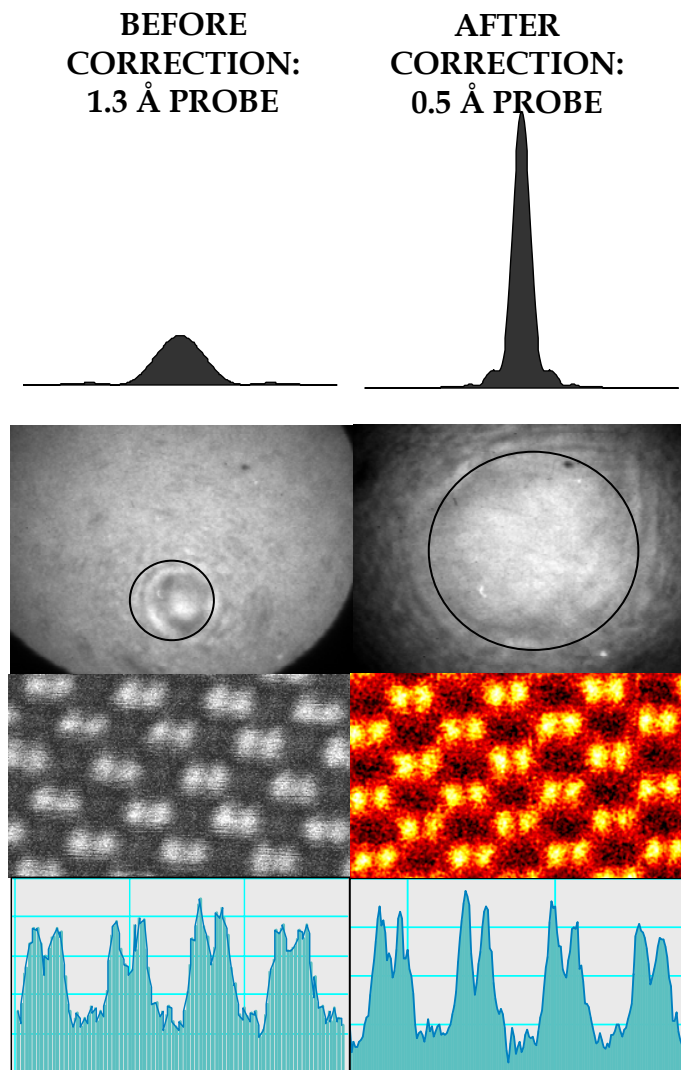
2.2.2 Analysis of the Pt/γ-alumina catalytic surface and discovery of OH-capped Pt trimers. [Results reported in: 9]

The Pt/γ-alumina surface was chosen for study because it is an archetypical heterogeneous catalytic system. For example, catalytic reduction and oxidation of automotive pollutants is accomplished with platinum (Pt) or rhodium (Rh) dispersed on a γ-alumina surface. Olefin cracking is also carried out on catalysts formed by dispersal of transition-metal atoms on an insulating support, such as a zeolite or alumina. In order to investigate the atomic-scale details of the active sites we have imaged a Pt/alumina catslyst. The image displayed in Fig. 8 shows isolated Pt atoms, Pt_2 dimers and Pt_3 trimers. The trimers of Pt are observed with preferred shapes that are inconsistent with those of gas-phase transition metal clusters and exhibit atypical Pt-Pt distances. We therefore carried out first-principles studies to identify the origins of the Pt clusters. These studies reveal three key features of the Pt/γ-alumina system: 1) Oxygen termination of the alumina surface is favored. 2) Adatom Pt structures are thermodynamically preferred over substitutional Pt structures. (i.e. Pt atoms in general do not fill surface Al or O vacancies.) 3) Pt_3 structures with anomalously long Pt-Pt distances are stabilized by -OH caps.
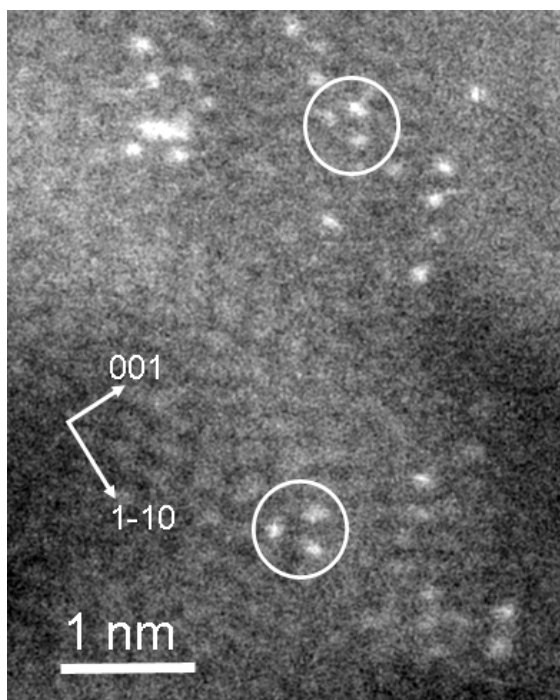
Figure 8. Image of Pt trimers on γ-alumina taken with the 300 kV VG Microscopes HB603U STEM. Note that the Pt-Pt distances are: 2.7 ± 0.2, 3.2 ± 0.2, and 3.4 ± 0.2 Å, which are inconsistent with typical Pt-Pt distances in most known Pt compounds of ca. 2.6-2.7 Å.

Mulliken population analysis of the first-principles wavefunctions showed that Pt atoms in the -OH capped Pt trimer on the oxygen-terminated surface bear significant valance unsaturation. While the actual charges determined by population analysis are only qualitatively reliable, taking electron depletion as a signature of Lewis acidity, it is reasonable to conclude that the supported clusters should be better Lewis acid sites than isolated Pt adatoms because the former show greater valance unsaturation. Charge density analysis also gives insight into the origin of the anomalous Pt-Pt distances. Elongation of the Pt-Pt bonds when the Pt_3 structure is -OH capped results from a flow of electron from the Pt to the cap, thereby weakening the Pt-Pt bonds. This effect is visible in Fig. 9, which shows electronic density in the Pt_3 plane with and without the capping -OH group. The intensity scale is thermal, with red indicating the greatest electron density. Note the significant depletion of electron

density between Pt atoms when the structure is -OH capped. We see a clear indication of depletion of electron density from the Pt-Pt bonds when the structure is -OH capped.

Figure 9. Upper images: Top down view of Pt_3/γ-alumina (left) and Pt_3OH/γ-alumina (right). Lower images: Electronic density (thermal scale, red=high) in the Pt Pt_3 plane corresponding to the image immediately above. Note the depletion of electron density in the Pt-Pt bonds when the structure is -OH capped.
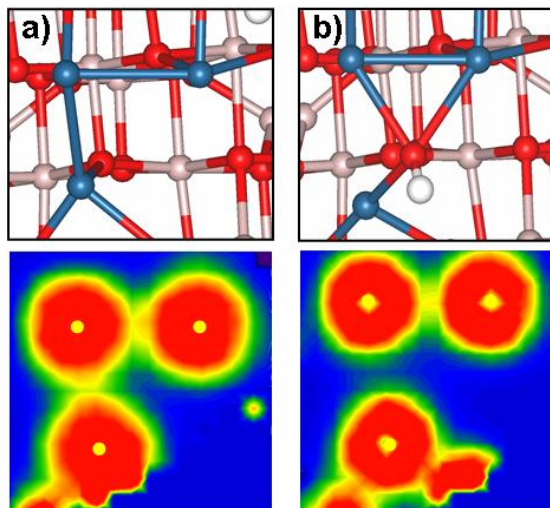
**2.2.3** Analysis of PtO_2. [Results reported in: 11]

Our discovery that Pt clusters on the alumina surface are partially oxidized indicated to us that an atomic-scale description of the structures of platinum oxides would be of great value in understanding Pt-containing heterogeneous catalysts. We therefore carried out a theoretical study of four proposed phases of PtO_2 using first-principles based thermodynamics and studied their inter-conversion with first-principles based kinetics.

Published experimental studies had provided some evidence for the existence of three polymorphs of PtO_2. These are: α-PtO_2 (CdI_2-type structure) [L. Maya, L. Riester, T. Thundat, C.S. Yust, *Journal of Applied Physics* 84, (1998) 6382], β-PtO_2 ($CaCl_2$-type structure) [A.N. Mansour, D.E. Sayers, J.W.C. Jr., D.R. Short, R.D. Shannon, J.R. Katzer, *Journal of Physical Chemistry* 88, (1984) 1778] and β′-PtO_2 (rutile-type structure) [M.P.H. Fernandez, B.L. Chamberland, *Journal of Less-Common Metals* 99, (1984) 99]. The existence of PtO_2 in a marcasite-type structure had also been suggested [O. Muller, R. Roy, *Journal of the Less-Common Metals* 16, (1968) 129]. We carried out a detailed and systematic first-principles study of the structures of these several proposed phases of PtO_2, their relative thermodynamic stability and the kinetics of their interconversion.

Based on first-principles calculations, we found that the α-phase of PtO_2 is thermodynamically favored at low pressure while the β-phase is favored at high pressure. By comparison with earlier theoretical results based only on calculations of the electronic energy, we found that the inclusion of vibrational contributions to the free energy is essential to correctly predict the relative stability of the α- and β-structures. The calculations further show that PtO_2 in the marcasite-type structure does not exist and that the β′-structure either represents an unstable fixed point (saddle point) on the potential energy surface or is just barely bound. While never thermodynamically favored, the β′-structure may represent an appreciable fraction of a PtO_2 sample. Although the high-pressure β-phase is thermodynamically unstable with respect to the α-phase at low *P*, it is a true metastable phase owing to a large energy barrier to their inter-conversion, and is kinetically stable over a wide temperature range.

2.2.4 Analysis of the Cr/γ-alumina catalytic surface and discovery of the reason for the dramatic difference in durability between the Cr/γ-alumina and Cr/η-alumina catalytic systems. [Results reported in: 5]

Chromia/alumina catalysts are widely used for industrial dehydrogenation of alkanes[S. De Rossi, G. Ferraris, S. Fremiotti, E. Garrone, G. Ghiotti, M. C. Campa, and V. Indovina, *J. Catalysis* 148 (1994) 36; B. M. Weckhuysen and R. A. Schoonheydt, *Catal. Today* 51 (1999) 223 (1999); R. L. Puurunen, B. G. Beheydt, and B. M. Weckhuysen, *J. Catalysis* 204 (2001) 253.] according to the reaction,

$$C_nH_{2n+2} \rightarrow C_nH_{2n} + H_2.$$
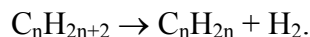
In this process different transition aluminas have been used as the catalytic support. At the present time, however, η-alumina is the preferred support in industrial processes because the catalysts Cr/η-alumina can last up to 2-3 years without significant degradation [R. Iezzi et al., "Process for Obtaining Light Olefins by the Dehydrogenation of the Corresponding Paraffins," US Patent No. 6,362,385 (March 26, 2002)]. At the same time, the analogous catalytic system based on γ-alumina degrades within a few weeks. The active chromium atoms disappear from the surface and have a tendency to form aluminum chromates. This considerable difference in degradation rate for catalysts using γ- versus η-alumina supports is quite puzzling because the two support materials have very similar crystalline bulk structures, differing essentially only in the distribution of cation vacancies.
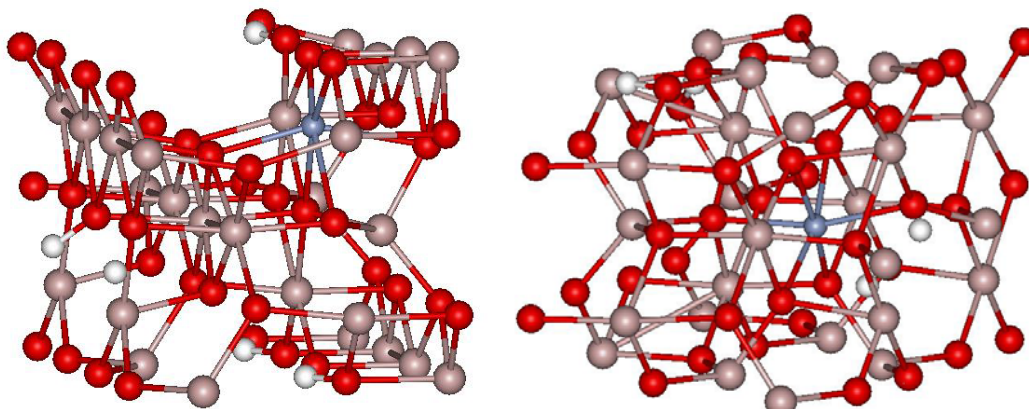
Figure 10. Cr atom (blue) adsorbed into a subsurface layer of γ-alumina (left) and η-alumina (right). The barrier to adsorbtion into η -alumina is about 2x higher.

We carried out first-principles calculations of Cr atoms on the surfaces of both γ- and η-aluminas. As both of these systems are known to exhibit catalytic activity, not surprisingly, it was found that at both surfaces Cr is highly active and can participate in catalytic reactions. It was also found that in both systems it is energetically favorable for Cr to occupy a subsurface layer position where it becomes six-fold coordinated. *The activation barrier for Cr to enter such positions, however, is much higher in the case of*

η-alumina. The activation barrier for Cr entering γ-alumina bulk is only 2.2 eV, as compared to 4.5-6 eV in η-alumina. (See. Fig. 10)

An important consequence of this result is that Cr can sustain its catalytic activity at the η-alumina surface for a very long time, while becoming completely deactivated on the γ-alumina surface within several days.

2.2.5 Interactions of small molecules (alcohols, hexane) with γ-alumina.
2.2.5.1 alcohols [Results reported in: 2]

The catalytic properties of alumina for alcohol dehydration have been exploited for more than 200 years [H. Knözinger, Angew. Chem. Internat. Edit. 7 (1968) 791]. Today, alcohol dehydration with alumina-based catalysts to form olefins and/or ethers for starting materials is an important industrial process. Future applications of alcohol dehydration catalysts could include the conversion of biomass-derived alcohols into transportation fuels and other energy products. While the complexity of heterogeneous catalysts for alcohol dehydration continues to increase as the technology advances, dehydration on transitional aluminas remains a prototypical reaction of alcohol dehydration by heterogeneous catalysis. We therefore have pursued an atomic-scale understanding of the reaction pathways to facilitate the design of improved catalysts.

Although different views are held concerning the mechanism of the heterogeneously catalyzed dehydration of alcohols on aluminum oxide, it is generally believed that the mechanism initiates with the direct interaction of the hydroxyl group of the alcohol with the oxide surface. Acidic and/or basic surface sites are assumed to take part in the dehydration procedure. At least three possible hydrogen-bonding interactions are easily envisioned, active H-bonding, passive H-bonding, and a bridging structure involving both active and passive H-bonding. Another chemically obvious interaction is through a four-center structure whereby the O atom of the alcohol OH interacts with a surface Lewis acid site (surface Al), and the OH proton interacts with a Lewis base site (surface oxygen).

To test these hypotheses we carried out calculations designed to investigate the preferred adsorption sites for alcohols on γ–alumina (110C) surfaces using an $Al_{48}O_{72}$ cluster model of γ–alumina that includes all atoms up to and including second-nearest neighbors of the adsorption site. We found that all four alcohols studied chemisorb to the alumina surface when they come close to the surface with suitable orientation. Only hydrogen of the alcohol OH group is required to interact with surface oxygen for successful dehydrogenation when the surface oxygen is close to a cation vacancy. If there are no vacancies near the surface oxygen, both the alcohol oxygen and hydrogen must interact with the surface to achieve dehydrogenation. We also investigated two possible routes to alkoxide formation and found that the direct reaction of the alcohol with a Lewis acid site is a lower energy path than neucleophilic attack on the alcohol by a surface Lewis base.

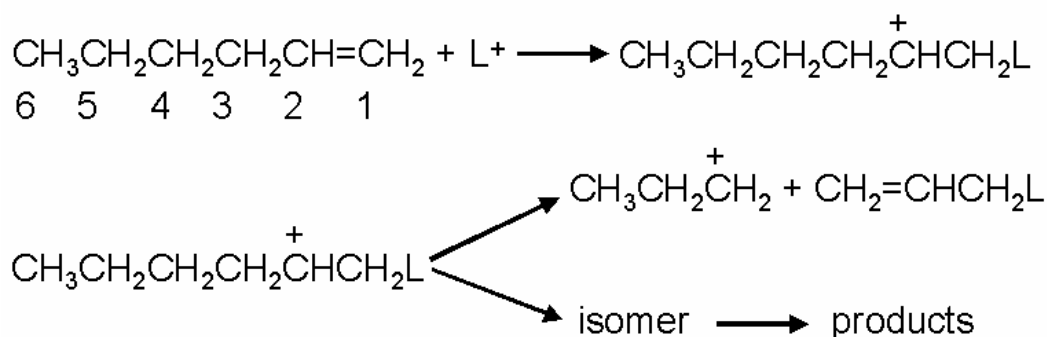Our calculations show that methanol, ethanol, propanol and isopropanol all chemisorb to the alumina surface when they come sufficiently close to surface with suitable orientation. The chemisorption is an exothermic process at a surface O site that has an adjacent Al vacancy and only O_s–H_{ad} interaction is required for successful dehydrogenation. At a surface O site where there are no adjacent vacancies both O_s–H_{ad}

and O_{ad}–Al interactions are required for successful dehydrogenation, that is, both the alcohol oxygen and hydrogen must interact with the surface. Calculations to investigate the interaction of two molecules at adjacent sites further verify this conclusion. This multi-point interaction means that one adsorbed molecule may block its neighbor from forming the four-center chemisorbed state required for dehydrogenation, implying that dehydrogenation is less than 100% efficient for high surface coverage. The site preference can be understood in terms of the alcohol hydrogen completing the valence of a surface O_s. The alcohol is acting as a Brønsted acid. Surface O_s atoms with adjacent vacancies serve as stronger Brønsted bases than those with no adjacent vacancies. These results provide the first atomic-scale description of the interaction of alcohols with heterogeneous catalysts.

2.2.5.2 hexene [Results reported in: 10]

Another prototypical application of alumina as a heterogeneous catalytic material is in olefin cracking and isomerization. The studies of Tung and Mcininch (TM) on the activity of high-purity alumina for 1-hexene conversion reactions showed that high-purity alumina possesses fairly good activity for 1-hexene cracking above 400 °C [S.E. Tung, E. Mcininch, Journal of Catalysis 3 (1964) 229; S.E. Tung, E. McInninch, Proc. Intern. Congr. Catalysis, 3rd, Amsterdam, North Holland Pub. Co.; New York, Interscience Publishers, 1 (1965) 687-710]. A plethora of products is produced. The observed gaseous cracking pattern of 1-hexene on alumina was explained by assuming the presence of two types of acid sites on alumina surfaces: Lewis acid sites and passive Bronsted acid sites. It was proposed that on alumina at 450 °C, hexene first cracks upon Lewis acid sites via a carbonium ion mechanism to form site-bound olefins. These, in turn, combine with hydrogen atoms to yield site-bound radicals. Further cracking then occurs via a free radical mechanism. Denoting the Lewis acid sites by L^+, cracking of hexene by this TM mechanism may be, in part, formally represented by Scheme I:

Scheme I

$$\underset{6\quad 5\quad 4\quad 3\quad 2\quad 1}{CH_3CH_2CH_2CH_2CH{=}CH_2} + L^+ \longrightarrow CH_3CH_2CH_2CH_2\overset{+}{C}HCH_2L$$

$$CH_3CH_2CH_2CH_2\overset{+}{C}HCH_2L \begin{array}{l} \nearrow CH_3CH_2\overset{+}{C}H_2 + CH_2{=}CHCH_2L \\ \\ \searrow isomer \longrightarrow products \end{array}$$

By contrast, in a study of skeletal isomerization of n-butene on alumina, Trombetta and co-workers suggested that C_4 olefins interact at room temperature with surface hydroxy groups on alumina (Scheme II) [M. Trombetta, G. Busca, S.A. Rossini, V. Piccoli, U. Cornaro, Journal of Catalysis 168 (1997) 334]. Additionally, they suggested that olefins dissociate over Al^{3+}–O^{2-} "acidic" couples, giving rise to allyl species that are nearly covalently bonded to surface aluminum atoms (Scheme III). It was further suggested that at higher temperature, strongly bonded carbonaceous species grow

on the surface at the expense of the allyl species. (Two strong IR bands, at 1570 cm^{-1} and 1480 cm^{-1}, provided evidence of the presence of carboxylates.) This is quite different from the proposal of Tung and McInnich. A complete description of olefin interactions with alumina, in particular the roles of the surface acid and base sites, has not been definitively established. Such an atomic-scale understanding would be of considerable value in the design of improved catalysts.

Scheme II

We have carried out calculations designed to differentiate between the proposed hexane-alumina interaction schemes by investigating the preferred adsorption sites for 1-hexene on γ–alumina (110C) surfaces. We found that H atoms can be abstracted from numerous positions on hexene by surface oxygen when they come sufficiently close to the surface. The energy barriers to these different H-abstraction processes are comparable, (around 10–15 kcal/mol) with those for the dehydrogenation of a terminal H beyond the double bond or an allylic H being slightly lower than those for abstracting H from other positions. This result offers a possible explanation for the plethora of experimentally observed reaction products.

Scheme III
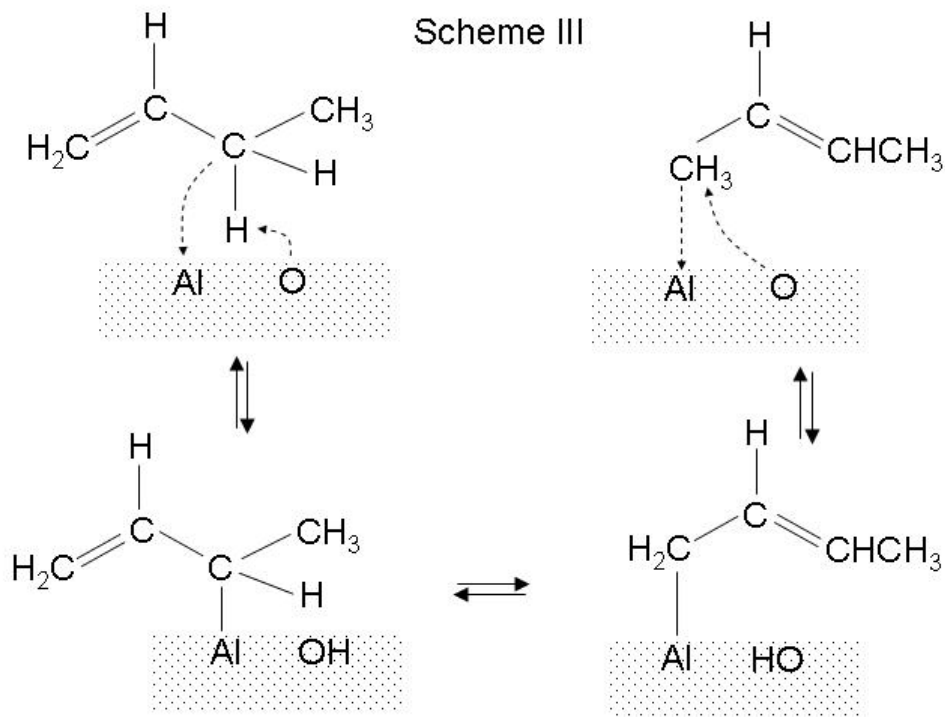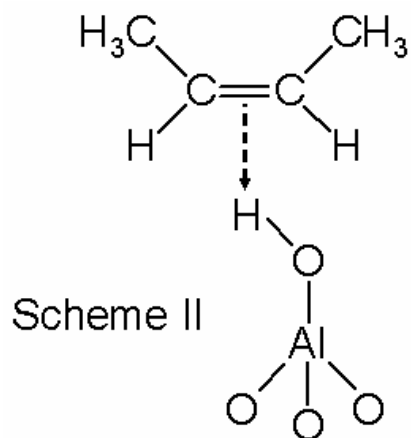
2.3 Objective 3) Address the question: What is the role of H in ceria? [Results reported in 1]

Cerium oxide (ceria) is a critical and multi-functional component of automotive emissions catalysts [A. Trovarelli, *Catal. Rev.-Sci. Eng.*, 38 (1996) 439]. One function of ceria is to act as an "oxygen storage" component. Ceria is capable of oxygen uptake during excursions of the air/fuel ratio into the net oxidizing regime, and oxygen release during excursions into the reducing regime, thus facilitating the maintenance of the proper stoichiometric ratio for sustained CO and HC oxidation and simultaneous NO_x reduction, i.e. *three way* catalysis (TWC) [K. C. Taylor, *Catal. Rev. - Sci. Eng.*, 35 (1993) 457].

Many of the key properties of ceria that contribute to its success in automotive catalysis are thought to arise from the fact that cerium has two stable oxidation states, Ce^{+3} and Ce^{+4}. [C. Lamonier, G. Wrobel, and J. P. Bonnelle, *J. Mater. Chem.*, 4 (1994) 1927] As a consequence, cerium oxide may exist over a range of possible stoichiometries CeO_{2-x} [$0 \leq x \leq 0.5$]. The deviation of ceria from its ideal CeO_2 composition has been extensively studied by temperature programmed reduction with hydrogen [C. Lamonier, A. Ponchel, A. D'Huysser, and L. Jalowiecki-Duhamel, *Catalysis Today*, 50 (1999) 247]. These studies have given rise to an important controversy: Is there hydrogen uptake by ceria upon reduction with hydrogen?

To determine the affinity of ceria for hydrogen, we considered the reaction:

$$HCe_4O_8 \rightarrow Ce_4O_8 + \text{½ } H_2.$$

Here Ce_4O_8 is used as the reference, instead of the empirical formula CeO_2, since the former is the formula for the primitive unit cell of cerium oxide. Employing DFT total energies to determine ΔH and tabulated third-law entropies to determine ΔS, we find that for the above reaction,

$$\Delta G = 0.45 - 6.768 \times 10^{-4} T,$$

where the energies are given in eV/molecule. This expression predicts that below 665K hydrogen uptake is spontaneous. Our calculations also predict that this uptake produces a lattice expansion of about 1.5 %. The H taken up forms hydroxide structures within the ceria bulk with a predicted vibrational frequency of 3414 cm^{-1}. These results are in good agreement with experimental reports. Our work, therefore, has resolved the issue of the thermochemistry of hydrogen uptake by ceria, finding that hydrogen uptake is spontaneous, but in sufficiently small quantities that it should be of minor consequence in catalytic systems.

2.4 Objective 4) Develop an atomic-scale description of photo-catalysts for water splitting. [Results reported in p9]

TiO_2 has been studied thoroughly both experimentally and theoretically since the discovery that it serves as a photocatlyst for water dissociation [K. Honda, A. Fujishima, *Nature* **238**, 37 (1972)]. Some outstanding puzzles remain, however, about its surface structure, photocatalytic activity and the influence of doping on its band gap. For example, the reason that Ti-vacancies are frequently observed between two O-vacancies in STM measurement [M. Li, W. Hebenstreit, L. Gross, U. Diebold, M.A. Henderson,

D.R. Jennison, P.A. Schultz, M.P. Sears, *Surf. Sci.* **437** (1999)] is not clear. Second, two distinct onsets are observed in the photoabsorption spectrum of carbon-doped TiO_2. The origin of this "double band gap" is unknown. The resolution of these puzzles would be helpful to better understand the structural and chemical properties of rutile TiO_2 and thereby suggest new schemes for doping TiO_2 for improved catalysis.

We carried out first-principles density-functional theory calculations and resolved the above outstanding puzzles about TiO_2. First, the calculations showed that because the Fermi level moves to the bottom of the nominal TiO_2 conduction band for the nonstoichiometric Ti-O-terminated surface, the removal of surface oxygen atoms forces the Ti valance electrons to occupy Ti $3d$ states in the CB. This explains why Ti vacancies are observed to occur adjacent to oxygen vacancies on the surface. The removal of one Ti atom for every two oxygen vacancies stabilizes the oxygen vacancies by removing the Ti valance electrons from the CB. Second, the calculations reveal the origin of the "double band gap" for C-doped TiO_2. The two observed onsets in the optical absorption spectrum arise from two occupied C $2p$ states within the nominal TiO_2 band gap. These results are shown schematically in Fig. 11.

Figure 11. Schematic representation of the electronic structure of pure and doped rutile. Left: TiO_2, Center: with surface oxygen vacancy, Right: with carbon doping. The valence band is principally oxygen $2p$ in character. The conduction band is principally Ti $3d$ & $4s$ in character. In the atomic limit, each TiO_2 unit contributes two filled oxygen $2p$ orbitals, four half-filled oxygen $2p$ orbitals, and four titanium valence

electrons. In the pure material, (left) the four titanium valence electrons fill the vacant oxygen $2p$ orbitals. When an oxygen atom is removed, (center) three oxygen $2p$ orbitals are removed, but only 4 electrons. The remaining two electrons are forced to reside in Ti $3d$ orbitals. Upon substitution of C for O, the carbon $2p$ bands "float up" into the band gap due to weaker nuclear-electron interaction. Onsets in the photoabsorption spectrum are seen corresponding to transitions from both occupied carbon $2p$ bands to the conduction band.
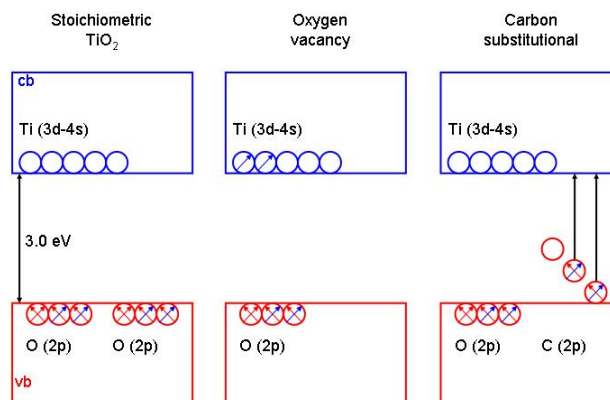
3. Supported personnel

The following personnel were directly support by this award:

- Dr. Karl Sohlberg: Lead PI. Assoc. Prof. of Chemistry at Drexel. Supported in the form of partial summer salary and travel.
- Prof. Sokrates T. Pantelides: co-PI. Prof. of Physics at Vanderbilt University. Supported in the form partial summer salary.

- Dr. Shuhui Cai: P.R.C. Visiting research scholar at Drexel University working with Karl Sohlberg. (permanent position - Prof. of Physics at Xiamen University) Supported by full salary and travel when at Drexel.
- Dr. Xiliang Nie: Half-time Instructor in the Chemistry Department at Drexel University and a half-time postdoctoral fellow working with Prof. Sohlberg. Supported by partial salary and travel.
- Dr. Sergey Rashkeev: Research Associate Prof. at Vanderbilt University. Supported by partial salary and travel.
- Dr. Albina Borisevich: Postdoctoral fellow working with Dr. Pennycook. Supported by partial salary.
- Dr. Xiange Zheng: Postdoctoral fellow working with Prof. Sohlberg. Supported by partial salary and travel.
- Dr. Shuping Zhuo: Postdoctoral fellow working with Prof. Sohlberg. Supported by full salary and travel.
- Mr. Ari B. Silver: Undergraduate research assistant working with Karl Sohlberg. Supported by partial salary and travel.
- Mr. John Ash: Undergraduate research assistant working with Sokrates Pantelides. Supported by partial salary.

4. Supported travel

This award funded travel by the personnel of this research program to disseminate results and to coordinate the three-institution collaboration:

- Karl Sohlberg: Fall 2001 MRS national meeting.
- Shuhui Cai: Vanderbilt University to meet with Sokrates Pantelides and Sergey Rashkeev to discuss mechanisms of alumina transformations.
- Shuhui Cai: March 2002 APS national meeting to present a contributed paper and meet with Sergey Rashkeev.
- Shuhui Cai: Spring 2002 MRS national meeting to present a contributed talk.
- Sergey Rashkeev: March 2002 APS national meeting to present a contributed paper and meet with Shuhui Cai.
- Sergey Rashkeev: Drexel University to meet with Karl Sohlberg, present a seminar and to outline and draft the manuscript reporting the Cr/alumina research.
- Karl Sohlberg: 2002 International Conference on Composites Engineering to deliver an **invited talk** on the subject of complex aluminas
- Karl Sohlberg: Fall 2002 MRS national meeting to present a contributed paper and meet with Sergey Rashkeev. He was accompanied by several members of his research group to provide them with a national meeting experience.
- Sergey Rashkeev: Fall 2002 MRS national meeting to present a contributed paper and meet with Karl Sohlberg.
- Sergey Rashkeev: March 2003 APS national meeting to present a contributed paper.
- Xiliang Nie: Vanderbilt University to meet with Sokrates Pantelides and Sergey Rashkeev to coordinate research on photocatalysts.
- Xiliang Nie: Fall 2003 MRS national meeting to present a contributed paper.

- Sokrates Pantelides: *Modelling Statistics and Dynamics in Catalysis Conference,* Schloss Ringberg, Germany, to deliver an **invited talk** September 2003.
- Stephen Pennycook: *Tri-State Catalysis Society Spring Symposium*, Louisville, Kentucky, to deliver an **invited talk** May 12 – 13, 2003.
- Karl Sohlberg: March 2004 APS national meeting to deliver an **invited talk** on complex catalytic materials and to meet with Sokrates Pantelides. He was accompanied by several members of his research group to provide them with a national meeting experience.
- Karl Sohlberg: Vanderbilt University for **invited VINSE seminar** and to meet with Sokrates Pantelides and Sergey Rashkeev.
- Shuping Zhuo: Fall 2004 MRS national meeting to deliver a contributed talk. The associated paper won the **Symposium Best Paper Award**.
- Albina Borisevich: *Microscopy and Microanalysis Annual Meeting*, Savannah, Georgia, to deliver an **invited talk** August 1 – 5, 2004.
- Shuping Zhuo: March 2005 APS national meeting in Los Angeles to deliver a contributed poster.
- Stephen Pennycook: *Division of Fuel Chemistry for the 229th ACS National Meeting*, San Diego, CA, to deliver an **invited talk** March 13 – 17, 2005.
- Sergey Raskkeev: *The Ψk 2005 Conference*, Schwäbisch Gmünd, Germany, to deliver an **invited talk** September 17 – 21, 2005.
- Sokrates Pantelides: *20th Panhellenic Conference of Solid State Physics and Materials Science*, Nicosia, Cyprus, to deliver an **invited talk** August 2005.

Co-PI's Pennycook and Pantelides delivered numerous talks and attended numerous meetings during the award period, but their travel was supported by other sources. All contributions are listed in the "Scientific products" section below.

5. Publications resulting from this research program

Journal publications:
[12] P.D. Nellist, M. F. Chisholm, N. Dellby, O.L. Krivanek, M. F. Murfitt, Z. S. Szilagyi, A. R. Lupini, A. Borisevich, W. H. Sides, S. J. Pennycook, "Direct Sub-Angstrom Imaging of a Crystal Lattice", *Science* **305,** 1741 (2004).
[11] Shuping Zhuo and Karl Sohlberg*," Platinum dioxide phases: relative thermodynamic stability and kinetics of inter-conversion from first-principles," *Physica B*, (in press).
[10] Shuhui Cai and Karl Sohlberg[*], "Adsorption of 1-hexene on γ–alumina (110C)," *J. Molec. Catal. A*, (in press).
[9] Karl Sohlberg*, Sergey Rashkeev, Albina Y. Borisevich, Stephen J. Pennycook and Sokrates T. Pantelides, "Origin of anomalous Pt-Pt distances in the Pt/alumina catalytic system," *ChemPhysChem*. **5**, 1893-1897 (2004).
[8] Sanwu Wang, Albina Y. Borisevich*, Sergey N. Rashkeev, Michael V. Glazoff, Karl Sohlberg, Stephen J. Pennycook and Sokrates T. Pantelides, "Dopants Adsorbed as Single Atoms Prevent Degradation of Catalysts," *Nature Materials*, **3**, 143-146 (2004).
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Computational Nanotechnology, (in press).

[6] Shu-Hui Cai, Sergey N. Rashkeev, Sokrates T. Pantelides, and Karl Sohlberg*, "Phase transformation mechanism between γ– and θ–alumina," *Phys. Rev. B*, **67**, 224104 (2003).

[5] S. N. Rashkeev*, K. Sohlberg, M. V. Galzoff, J. Novak, S. J. Pennycook and S. T. Pantelides, "Transition metal atoms on transition alumina phases: the role of subsurface sites on catalytic activity," *Phys. Rev. B*, **67**, 115414 (2003).

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[2] Shuhui Cai and Karl Sohlberg*, "Adsorption of alcohols on γ–alumina (110C)," *J. Molec. Catal. A*, **193**, 157-164 (2003).

[1] Karl Sohlberg*, Sokrates T. Pantelides and Stephen J. Pennycook, "Interactions of hydrogen with CeO_2," *J. Am. Chem. Soc.*, **123**, 6609 (2001).

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[p22] A. Y. Borisevich, A. R. Lupini, S. Rashkeev, S. Wang, G. M. Veith, N. J. Dudney, S. T. Pantelides and S. J. Pennycook, "Aberration-Corrected STEM for Understanding the Catalytic Mechanisms and Development of New Catalysts," p. 218 in *Proceedings of Microscopy and Microanalysis 2005*, Microsc. Microanal. 11(Suppl 2), 2005, Cambridge University Press, Cambridge, United Kingdom, 2005.

[p21] A. Y. Borisevich, A. R. Lupini, S. Wang, S. N. Rashkeev, S.T. Pantelides, K. Sohlberg and S. J. Pennycook, "Single-Atom Sensitivity for Solving Catalysis Problems", p. 460 in the Proceedings of Microscopy and Microanalysis 2004 (*Microscopy and Microanalysis*, Vol.10, Suppl.2, 2004), eds. I. M. Anderson, R. Price, E. Hall, E. Clark, and S. McKernan, Cambridge University Press, Cambridge, United Kingdom, 2004.

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[p18] Shuping Zhuo and Karl Sohlberg, "*P-T* phase diagram for Rh(III) oxides from first principles," Ninth National Symposium of Quantum Chemistry of China, Guilin, China, 8-12 October (2005).

[p17] Sanwu Wang, A.Y. Borisevich, S.N. Rashkeev, M.V. Glazoff, K. Sohlberg, S.J. Pennycook and S.T. Pantelides, "Atomic Scale Catalysis: Structure and Reactions of

Chromium Oxide Species on Transition Aluminas," Annual APS March Meeting 2005, Los Angeles, California, L20.00006.

[p16] Shuping Zhuo and Karl Sohlberg, "P-T phase diagram for Rh(III) oxides from first principles," Annual APS March Meeting 2005, Los Angeles, California, C1.00096.

[†p15] Shuping Zhuo and Karl Sohlberg, "The thermodynamic stability of three near-degenerate phases of platinum dioxide," Materials Research Society Proceedings: Solid-State Chemistry of Inorganic Materials V, FF7.8 (F2004).

[p14] Shuping Zhuo and Karl Sohlberg, "First-principles studies of structures and phase transitions of platinum dioxides," *Abstracts of papers of the American Chemical Society*, **228**: PHYS-366.

[p13] Shuping Zhou and Karl Sohlberg, "First-principles studies of structures and phase transitions of platinum dioxides," *Drexel Research and Venture Day 2004*, #127P.

[p12] S. N. Rashkeev, Sanwu Wang, A. Y. Borisevich, S. J. Pennycook, M. V. Glazoff, K. W. Sohlberg, S. T. Pantelides, *"Stabilization of γ-alumina catalyst by adsorbed La atoms*," *Annual APS March Meeting 2004, Montreal Canada*, Z21.008.

[p11] Albina Borisevich, Sergey Rashkeev, Sanwu Wang, Michael Glazoff, Karl Sohlberg, Stephen Pennycook, Sokrates Pantelides, *"Effect of dopant distribution on aging of catalytic Cr-doped transition aluminas*," *Annual APS March Meeting 2004, Montreal Canada*, Z21.007.

[p10] Karl Sohlberg, "Catalytic aluminas: insights from first-principles calculations" *Annual APS March Meeting 2004, Montreal Canada*, H5.001.

[†p9] Xiliang Nie and Karl Sohlberg, "The Influence of Surface Reconstruction and C-impurities on Photocatalytic Water Dissociation by TiO2," *Materials Research Society Symposium Proceedings: Hydrogen Storage Materials*, 801, BB6.6 (2003).

[p8] Xiliang Nie and Karl Sohlberg, "Ab initio exploration of the mechanism for photoelectrochemical splitting of water," *Drexel Research Day 2003*, #54.

[p7] S.N. Rashkeev, K. Sohlberg, M.V. Glazoff, J. Novak, S.J. Pennycook, S.T. Pantelides, "Transition metal atoms on different alumina phases: The role of subsurface sites on catalytic activity," *Annual APS March Meeting 2003, Austin, TX*, X25.002.

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[†p4] S. N. Rashkeev, K. Sohlberg, M. V. Glasov, J. Novak, S. J. Pennycook and S. T. Pantelides, "Chromium and Lanthanum on Transition Alumina Surfaces: The role of bulk point-defect distributions on catalytic activity," *Materials Research Society Symposium Proceedings: Structure-Property Relationships of oxide Surfaces and Interfaces II*, Z2.7 (F2002).

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[†p2] Shu-Hui Cai and Karl Sohlberg, "Migration of Aluminum Atoms in the Transformation of γ– to θ–Alumina," *Materials Research Society Symposium Proceedings: Modeling and Numerical Simulation of Materials Behavior and Evolution*, **731**, W3.6 (2002).
[p1] Shuhui Cai, Karl Sohlberg, Sergey Rashkeev and Sokrates T. Pantelides, "Transformation of γ-alumina to θ-alumina," *March meeting of the APS, Indianapolis, IN 2002*, # H33.004.

7. Conclusions

    Important results from this research (and the corresponding published works) include:

- A detailed atom-by-atom description of the mechanism by which γ-alumina transforms to θ-alumina at elevated temperatures [4,6].
- An explanation of the mechanism by which La stabilizes γ-alumina with respect to sintering at high temperature [8].
- An explanation of the anomalous structure of Pt_3 clusters observed on the surface of Pt/γ-alumina catalysts and the origins of their catalytic activity [9].
- A first-principles based thermodynamic analysis of the phases of PtO_2 and demonstration that the inclusion of vibrational contributions to the free energy is essential to correctly predict the relative stability of the structures. In addition it was found that the rutile structure is not a stable "phase" but represents an unstable fixed point on potential energy surface [11].
- A demonstration of how a subtle difference between the distributions of bulk defects in two ubiquitous catalytic materials, Cr/γ-alumina and Cr/η-alumina, gives rise to qualitatively different surface chemistries and thermal stability [2].
- Addressing decades-old questions about the initiation step in the mechanism of alcohol dehydration on γ-alumina surfaces, a prototypical heterogeneous catalyst reaction [2].
- An atomic-scale description of the interaction of hexene with γ-alumina and elucidation of the reason that a plethora of reaction products are observed [10].
- Demonstration by first-principles calculations that only minor quantities of hydrogen are taken up by ceria during temperature programmed reduction [1].
- Explanation of the coincidence of oxygen and titanium vacancies in rutile TiO_2 and explanation of the "double band gap" feature in the photoadsorption spectrum [p9].