

**Crystal Phases, Microstructure and Surface Chemistry of Industry-Relevant  
Nanostructured Metal Oxides\***

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**Crystal Phases, Microstructure and Surface Chemistry of Industry-  
Relevant Nanostructured Metal Oxides**

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I. Introduction

Industries response keenly to two factors: the costs of materials and processing, and regulatory forces imposed by governments. The method of neutron scattering may be applied to address these concerns. Slow (cold to epithermal) neutrons probe the organization and dynamic response of atomic nuclei and electrons in a substance thereby providing valuable knowledge toward the development of cost-effective means for materials preparation and possessing. Neutron facilities for basic research are funded by governments, thus these organizations are obliged to provide technical support to industries for the fulfillment of governmental policies. I hope to argue, based on these premises, the mutual beneficialness of a close collaboration between the industrial-research and neutron-scattering communities. In order to limit the scope of discussion, I shall illustrate the potential applications of neutron scattering for industrial problems by some recent studies of nanostructured metal-oxide catalysts.

II. Three-way catalysts for automotive emission control

The automobile industry is faced with a pressing demand for a total removal of hydrocarbons (HC), carbon monoxide and nitrogen oxide pollutants from automotive emission. The performance of the present three-way catalytic converters, which consist of precious metals such as Pt and Rh dispersed on high-surface-area alumina, zirconia and ceria washcoats, have to be dramatically improved. In order to simultaneously reduce NO<sub>x</sub> and oxidize CO and HC effectively, the car engine has to maintain dynamically an air-to-fuel mass ratio to within a narrow window. Moreover, concerns of global warming due to the green-house effect have led to the imposition of limited CO<sub>2</sub> emission. This requires a shift of the air-to-fuel ratio to the so-called "lean-burn" condition, under which the

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current three-way catalysts are unable to remove the pollutants, particularly NO<sub>x</sub>, satisfactorily. Our neutron-scattering studies of rare-earth (RE) modified nanostructured zirconias and aluminas in collaboration with M. Ozawa (formerly of Toyota Co.) and S. Suzuki of Nagoya Institute of Technology aim for an understanding of their crystal phases, microstructure and surface chemistry towards an eventual development of better three-way catalysts.<sup>1</sup>

### III. Particle Growth in Sol-Gels, Fig. 1 a-b.

Fine powders of metal oxides produced by industrial methods usually contain microstructure. An understanding of the molecular and crystalline assemblage of the basic building blocks is essential to the development of cost-effective processing of materials with tailored properties. In the case of RE-modified zirconia prepared by coprecipitation from an aqueous solution of ZrOCl<sub>2</sub> and RECl<sub>3</sub>, it is thought that the conditions effecting the polymerization and nucleation of the hydrolyzed [Zr<sub>4</sub>(OH)<sub>8</sub>•16(H<sub>2</sub>O)]<sup>8+</sup> tetramers directly influence the nanostructured nature of the powders. Small-angle neutron scattering (SANS) enables the characterization of particle growth and size distribution within a medium of sizes up to about 500 nm. From the slope of the SANS profiles (log-Intensity versus log-Q where Q is the neutron wavevector), a fractal dimension which is characteristic to the particle-growth mechanism can be identified with the pH value of a zirconia solution.<sup>2,3</sup> The microstructure in terms of primary-particle size, surface area, porosity, and nature of aggregation of the zirconia powders, with and without RE doping, can be described by a mass-fractal model.<sup>4</sup> The pure ZrO<sub>2</sub> powder dried at 290°C exhibits microporosity and high surface area initially. Subsequent heat treatment rapidly converts microporous structure to mesoporosity with a mass-fractal-like aggregation.<sup>5</sup> At about 600°C, however, the aggregate transforms from fractal-like to random packing of well-grown, relatively smooth particles which results in large reduction of surface area due to collapse of mesopores to macroporous structure. The Nd- and Ce-modified zirconia, on the other hand, retain the fractal geometry and mesoporosity after annealing at 600°C. Substituting Zr with ~10 mol% of Nd to form a solid solution of rare-earth oxide and zirconia retards particle sintering and preserves the large surface area and thermal stability needed for catalytic functions. Therefore, the SANS results provided a basis for the effective utilization of RE-modified zirconias by industry.

### IV. Oxygen-Vacancy Induced Defects and Metal-Support Interaction, Fig. 1c.

It is well known that pure zirconia has at least three crystal phases: monoclinic, tetragonal and cubic structures at low ( $T < 1400\text{K}$ ), medium ( $1400 < T < 2460\text{K}$ ) and high ( $T > 2460\text{K}$ ) temperature, respectively. A partial substitution of the zirconia atoms with RE elements has two major effects: 1) the high-temperature phases can be stabilized down to room temperature thereby removing the disruptive phase transformations and increasing thermal stability; and 2) if the dopant RE ions are trivalent such as  $\text{Nd}^{3+}$ , oxygen vacancies are generated in order to maintain electroneutrality of the lattice. Under an oxygen pressure gradient, ionic charges can migrate via the oxygen vacancies thus generating an emf difference. This property of zirconia electrolytes has led to commercial applications such as exhaust-gas oxygen sensors in automobiles. This type of defect structures are well suited for neutron-diffraction studies because, unlike x-rays, the neutron coherent scattering cross section of O is comparable to that of Zr, providing the necessary sensitivity to subtle O displacements. Using neutron powder diffraction, the crystal structure of high-surface-area  $\text{Ln}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$  ( $\text{Ln} = \text{La}$  and  $\text{Nd}$ ) were found to be composed of mixed phases of tetragonal and cubic symmetry which can be stabilized over a temperature range (up to  $\sim 1000^\circ\text{C}$ ) pertinent to catalytic applications.<sup>6,7</sup> A real-space correlation function, obtained from a Fourier transform of the filtered residual diffuse scattering, showed evidence of static, oxygen vacancy-induced atomic displacements along the pseudocubic  $\langle 111 \rangle$  and other directions.

Next, the  $\text{Ce}^{3+} \leftrightarrow \text{Ce}^{4+}$  redox process in the Ce-ZrO<sub>2</sub>/Pt catalyst, which gives rise to additional oxygen storage/release capability under a dynamic air-to-fuel ratio cycling, was investigated by an *in-situ* diffraction experiment.<sup>8</sup> Such a function involves a metal-support interaction which is not completely understood. The interaction of platinum with ceria may be rationalized by a model which involves associative adsorption of CO on Pt/CeO<sub>2</sub> followed by a reaction to produce CO<sub>2</sub> and an oxygen vacancy.<sup>9</sup> During this process oxygen is released and Ce 4+  $\rightarrow$  3+ transition occurs. Since the difference in the ionic radius of Ce<sup>4+</sup> (0.80 Å) and Ce<sup>3+</sup> (1.01 Å) is substantial, a change of the lattice cell volume of the oxide is expected if the transition involves Ce ions *in the bulk*. The samples, 10 mol% Ce-doped zirconia with and without Pt (1 wt%) impregnation, were heated first in flowing 2%O<sub>2</sub>/Ar from room temperature to 400° C and then in 1%CO/Ar to about 700° C. A discontinued increase of the tetragonal unit-cell volume, a decrease of tetragonality, and a change of color from light yellow to gray when changing from oxidizing to reducing atmosphere were observed only in the sample containing Pt. This result supports the model which assumes the

formation of oxygen vacancies initially near the Pt atoms. As more Ce ions are reduced from 4+ to 3+ oxidation states at high temperatures, oxygen vacancies migrate to the bulk of the oxide particles.

#### V. Vibrations of Atoms and Adsorbed Molecules, and Structure of Interfaces, Fig. 1 d-f.

It is well known that neutrons, unlike laser and infrared radiation, probe the vibrations of atoms over a wide range of energies and wavevectors not restricted by selection rules. This permits a measurement of the generalized (neutron scattering cross-section weighted) phonon density of states (PDOS) of crystalline and disordered materials and a straightforward comparison with results from lattice-dynamics modeling or molecular-dynamics simulations. We found distinct differences in the PDOS between the nanopowder and the bulk zirconias.<sup>10</sup> Since phonons are responsible for many important thermodynamic and mechanical properties. This information is useful to correlation the macroscopic behavior and microscopic properties in industrial processed materials.

Neutron spectroscopy can also benefit the study of the surface chemistry of high-surface-area powders, for example, monitoring the response of adsorbed molecules containing hydrogen - a direct consequence of the large incoherent scattering cross section of hydrogen. During an isosynthesis reaction over a zirconia catalyst where syn gases are converted into branched hydrocarbons, it is thought that the physisorbed and chemisorbed hydrogen and hydroxyl species play an important role in the intermediate reactions.<sup>11</sup> The dynamics of hydrogen atoms associated with the surface hydroxyl groups and adsorbed water molecules on  $\text{Ln}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$  and pure  $\text{ZrO}_2$  over a frequency range of 0-4400  $\text{cm}^{-1}$  was investigated by neutron inelastic scattering.<sup>7, 12</sup> The stretch vibrations of surface hydroxyl groups on monoclinic  $\text{ZrO}_2$  were found to have slightly higher frequencies than those for  $\text{Ln}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$ . At a submonolayer coverage of water the O-H stretch bands broaden and shift to lower energies. At higher coverage three bands, corresponding to the O-H stretch, H-O-H bend and librational motion of water molecules were observed, indicating the influence of hydrogen bonding. The neutron results can be compared with infrared data and *ab initio* calculations<sup>13</sup> for similar zirconia systems found in the literature. Similar investigations have also been conducted for physisorbed hydrogen molecules on Ce- and Nd-doped  $\text{ZrO}_2$ .<sup>14</sup>

Finally, deposition of semiconducting thin films is an important area in many branches of industry. Neutron reflectivity measurements provide unique information regarding the density variation

across an interfacial region. We may regard the technique of neutron reflection similar to microscopy. But, since neutrons can penetrate the substrate or surface layers and be reflected from an interior interfacial region, neutrons can survey a surface inside the bulk of materials, which optical or electron microscopy cannot. Preliminary neutron reflectivity measurements were carried out to study a spin-coated zirconia film on a silicon wafer.<sup>3</sup>

## VI. The Future

I hope the above examples have demonstrated the usefulness of various neutron-scattering techniques to vital industrial interests in materials characterization. However, as researchers from industries, universities and neutron facilities endeavor to develop advanced materials and novel techniques, much work remains to be done to bring these often independent, unconnected efforts closer to match the needs of each other. It is a pleasure to witness the recent heightened interactions among industries, academia and neutron societies. This Workshop is an excellent example.

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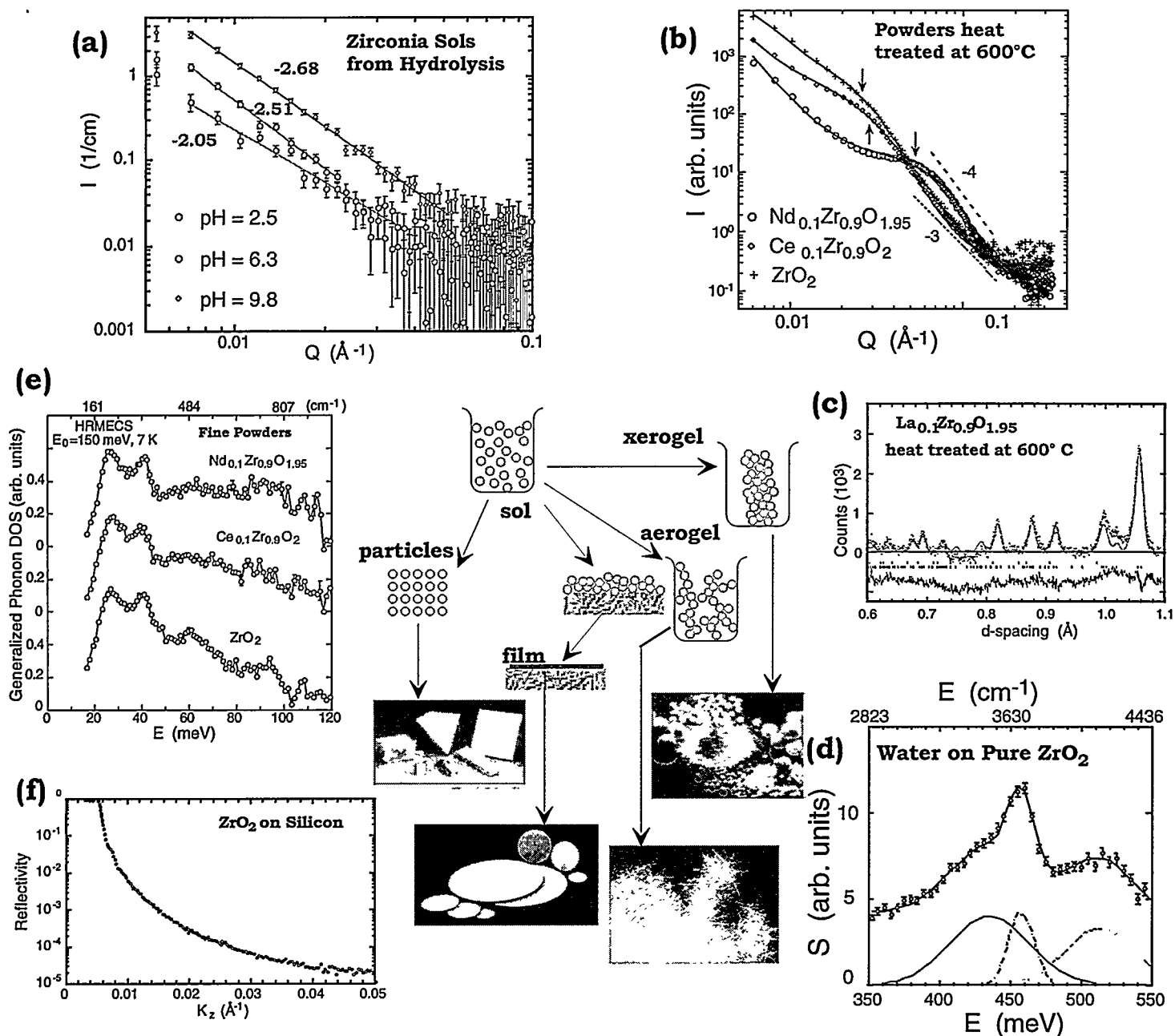


Figure 1. The center cartoon represents an industrial processing of materials, yielding a variety of products containing different microstructures. The method of neutron scattering can be applied to study the organization and dynamics of the microscopic building blocks of these materials. (a) The SANS profile of hydrolyzed zirconia sols at different pH values corresponding to distinct fractal dimensions. (b) The SANS of pure and RE-doped zirconia nanoparticles. The solid lines are the fits of the data to the fractal model. Limiting slopes for power-law behavior are given by the dotted lines. (c) Rietveld profile fit of neutron diffraction data for a La-modified zirconia. The dots are the observed, background-subtracted intensities. The solid line represent the calculated crystalline intensities. Tick marks of the top and bottom rows indicate the positions of the Bragg reflections for the cubic and tetragonal phases, respectively. The residual intensities display oscillatory deviations due to oxygen defects. (d) The O-H stretch vibration band and the combination band fitted to a sum of multiple Gaussian functions and a background for a monolayer of adsorbed water molecules on a pure zirconia powder. (e) The generalized phonon densities of states of pure and RE-doped zirconia powders obtained from inelastic scattering. (f) The observed neutron reflectivity from a zirconia film spin-coated on a silicon wafer.