Neutron and Raman scattering studies of surface adsorbed molecular vibrations and bulk phonons in ZrO$_2$ nanoparticles*

Masakuni Ozawa and Suguru Suzuki
CRL, Nagoya Institute of Technology, Tajimi, Gifu 507, Japan
C.-K. Loong and J. C. Nipko
IPNS, Argonne National Laboratory, Argonne, IL 60439, USA

*Work in Argonne is supported by the U.S. DOE-BES under Contact No. W-31-109-ENG-38

A paper (Ref No P72)
submitted to Proceedings of International Symposium on Surface Nano-control of Environmental Catalysts and Related Materials (6th Iketani Conference) at Nov. 25-27, 1996, Japan

Corresponding author and address:
Masakuni Ozawa
Nagoya Institute of Technology,
CRL, Asahigaoka, Tajimi, Gifu 507, Japan
Phone 81-572-27-6811,
FAX 81-572-27-6812,
email ozawa@crl.nitech.ac.jp
DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.
Abstract

Inelastic neutron-scattering method was applied to the study of the phonon densities of states of zirconia nanoparticles, the O-H stretch vibrations of physisorbed water molecules and chemisorbed hydroxyl groups on the surface. Raman scattering was also used to measure the zone-center phonon modes. The observed distinct phonon frequencies and band widths at 10-120 meV reflect the different crystalline symmetries and compositional fluctuations in the small grain and interfacial regions of monoclinic ZrO$_2$, tetragonal or mixed cubic and tetragonal rare-earth-modified zirconia. The dynamics of water and hydroxyl groups on varying local structures of these zirconias result in the different frequencies of the O-H stretch vibrations at 400-600 meV.

Keywords

zirconia; lanthanide; neutron scattering; Raman scattering; phonon density of state; hydroxy group
1. Introduction

Ultrafine lanthanide (Ln)-modified zirconia powders provide high surface areas and heterogeneous adsorption sites that are essential to catalytic functions. They are useful as catalytic components in automobile exhaust-emission-control systems and as methanol synthesis catalysts [1-3]. They are now industrially synthesized by a coprecipitation process using aqueous solutions of metal chlorides or other salts. A typical powder consists of aggregates of nanoscale (4-20nm) crystalline particles with ramified porous microstructure. Lanthanide dopants in zirconia stabilize the high-symmetry (cubic and/or tetragonal) crystal-phases over a wide range of temperatures pertinent to catalytic reactions. In addition, trivalent lanthanide ions such as La$^{3+}$ replacing Zr$^{4+}$ host cations have to be charge-compensated by oxygen vacancies in the lattice or OH species on the surface. Water and surface hydroxyl group play important roles in above-mentioned catalytic reactions.

Present study focuses on two aspects; the lattice dynamics of several pure and La-modified zirconia nano-structured powders, and vibrations of adsorbed OH and H$_2$O on the surface. Raman scattering is used to measure the zone-center phonon modes in monoclinic ZrO$_2$, tetragonal or mixed cubic and tetragonal Ln-modified zirconia. Unlike Raman scattering, neutron scattering by phonons is not restricted by selection rules [4]. The phonon densities of states of zirconia nanoparticles are studied by inelastic neutron scattering method (neutron spectroscopy). Furthermore, it is advantageous that neutrons are sensitive to vibrations of adsorbed OH and H$_2$O due to the large scattering cross section of hydrogen. We examined the O-H stretch vibrations of physisorbed water
molecules and chemisorbed hydroxyl groups.

2. Experimental

Pure ZrO\textsubscript{2} powders were synthesized by hydrolysis, and Ln-modified ZrO\textsubscript{2} powders of compositions, Ce\textsubscript{0.1}Zr\textsubscript{0.9}O\textsubscript{2} and Ln\textsubscript{0.1}Zr\textsubscript{0.9}O\textsubscript{1.95} (Ln=La and Nd) were prepared by a coprecipitation method as described in a previous study on catalytic supports [5,6]. Neutron diffraction data of ZrO\textsubscript{2}s were obtained at room temperature using General Purpose Powder Diffractometer (GPPD) in Intensed Pulsed Neutron Source (IPNS) of Argonne National Laboratory. X-ray diffraction data were collected using a powder diffractometer (Rigaku, model Rint, Japan) attached with Ni-filtered CuK\textalpha radiation in the range of 2\theta =20 to 90°. Their patterns were analyzed using multi-phase Rietveld fitting technique [8].

Inelastic neutron scattering experiments were performed using the High-resolution Medium-Energy Chopper Spectrometer (HRMECS) at IPNS. The energy resolution (full width at half maximum) is approximately 4 to 2 % of the incident energy, \textit{E\textsubscript{0}}, across the neutron energy-loss spectrum. For the incident energies, 50, 150, and 600 meV, were used to measure the phonon spectra at low temperature over the 0-550 meV range with good resolution [9]. Raman scattering spectra of ZrO\textsubscript{2} powders were measured by Raman spectrometer (Perkin Elmer, model RPM-1000, USA) using a Nd-YAG laser.

3. Results and discussion

3.1 Crystal phases and Raman scattering
Both the neutron and X-ray diffraction patterns of ZrO$_2$, Ce$_{0.1}$Zr$_{0.9}$O$_2$ and Ln$_{0.1}$Zr$_{0.9}$O$_{1.95}$ (Ln=La and Nd) showed considerably broadened peaks caused by internal strains, size incoherency and/or composition fluctuations of small crystalline grains. Rietveld refinements revealed a monoclinic structure for pure ZrO$_2$, a tetragonal structure for Ce$_{0.1}$Zr$_{0.9}$O$_2$, and a mixed cubic and tetragonal structure for Ln$_{0.1}$Zr$_{0.9}$O$_{1.95}$ (Ln=La and Nd). Furthermore, analyses of the zirconias by a Fourier filtering technique indicated the presence of short-range defect structure induced by oxygen vacancies as a consequence of charge compensation for the different cation valence within the lattice [6].

Figures 1 and 2 show the Raman scattering spectra for pure ZrO$_2$ and La$_{0.1}$Zr$_{0.9}$O$_{1.95}$ heated at various temperatures, respectively. In both materials, Raman lines sharpen with increasing heat-treatment temperature, as expected for the growth of crystallinity. However, the peaks are much sharper for ZrO$_2$ heat-treated at 1000°C as compared to the corresponding spectrum for La$_{0.1}$Zr$_{0.9}$O$_{1.95}$. This supports the notion that La-doping retards the particle growth by stabilizing a mixed cubic and tetragonal phases. The 12 peaks (638, 616, 560, 503, 476, 348, 335, 309, 222, 191 cm$^{-1}$) observed in ZrO$_2$ (Fig 1c) represent the strong Raman active modes expected for a monoclinic symmetry (9A$_{g}$ + 9B$_{g}$) [10]. The tetragonal phase of zirconia implies 6 Raman active modes (A$_{1g}$ + 2B$_{1g}$ + 3E$_{g}$) of which 4 strong peaks (635, 470, 330, 265 cm$^{-1}$) were observed in La$_{0.1}$Zr$_{0.9}$O$_{1.95}$ (Fig 2c). Our data are in general agreement with Raman spectra reported previously for pure and stabilized zirconias [11,12].
3.2 Neutron scattering for phonon

Unlike Raman scattering, neutron scattering from phonons is not restricted by selection rules, and the observed intensity includes phonon contributions (weighted by the neutron scattering cross sections of the constituent elements) throughout the Brilouin zone. In the present case, the neutron spectrum can be interpreted as a generalized phonon density of states (DOS) [13].

The observed spectra for pure ZrO$_2$, Ce$_{0.1}$Zr$_{0.9}$O$_2$ and Nd$_{0.1}$Zr$_{0.9}$O$_{1.95}$ heat-treated at 600°C (Fig 3) display a band consisted of peaks at 26, 30, and 40 meV and a broad band extending from 50 to $\sim$100meV. Our calculations using a lattice-dynamics model indicate that the low-energy band involves mainly motion due to Zr atoms, whereas the high-energy phonons involve mainly oxygen vibrations. It can be seen that the phonon densities below $\sim$50 meV in all three samples are similar but the high-energy band broadens and extends to higher energies progressively from pure ZrO$_2$ to Ce$_{0.1}$Zr$_{0.9}$O$_2$ to Nd$_{0.1}$Zr$_{0.9}$O$_{1.95}$. This feature suggests the force fields around the oxygen atoms in the latter materials are more dispersive. The interpretation for observed phonon are also supported by the structural feature that Ln(3+)-doping to the zirconia lattice induces a short-range defect structure confirmed by diffraction methods.

Furthermore, not only the three zirconias have distinct crystal structures, they exhibit different texture. From nitrogen adsorption isotherm measurements we find that the BET surface area and average pore radius of these powders heat-treated at 600°C are: 35.1 m$^2$/g, >100nm for ZrO$_2$; 26.1 m$^2$/g, 5 nm for Ce$_{0.1}$Zr$_{0.9}$O$_2$; and 72.3 m$^2$/g, 3 nm for Nd$_{0.1}$Zr$_{0.9}$O$_{1.95}$. Qualitatively, the influence
by these microstructures on the phonons manifests in the higher-energy oxygen vibrations (Fig 3). In pure ZrO\textsubscript{2} the large particle size and relatively more homogeneous grains give rise to narrower phonon bands. In Ce\textsubscript{0.1}Zr\textsubscript{0.9}O\textsubscript{2} and Nd\textsubscript{0.1}Zr\textsubscript{0.9}O\textsubscript{1.95}, on the other hand, compositional fluctuation and atomic disorder in the small crystallite and intergranular region result in the broadening of the higher-energy phonon band, which reflects the incoherency of oxygen motion in these nanostructural powders. Moreover, in the case of Nd\textsubscript{0.1}Zr\textsubscript{0.9}O\textsubscript{1.95}, oxygen vacancies and additional OH\textsuperscript{-} groups are present to compensate the valence difference between Nd\textsuperscript{3+} and Zr\textsuperscript{4+} ions. The increase in the phonon density to beyond 100 meV in Nd\textsubscript{0.1}Zr\textsubscript{0.9}O\textsubscript{1.95} is in part due to additional scattering from hydroxy groups. These results demonstrate that neutron-scattering measurements of phonon DOS for nano-particle zirconias are sensitive to the dynamics of lattice and interfacial atoms characteristics of underlying structures.

3.3 Neutron scattering for surface water and hydroxyl group

The large cross-section of neutron incoherent scattering for hydrogen yields a capability in probing the surface chemistry of nano-scale powders. Figure 4 shows the observed O-H stretch vibration bands of a submonolayer of adsorbed water on pure ZrO\textsubscript{2} and Nd\textsubscript{0.1}Zr\textsubscript{0.9}O\textsubscript{1.95}, obtained from inelastic scattering with \(E_0=600\) meV. Two O-H stretch frequencies corresponding to chemisorbed surface OH group (\(v_1\)) and physisorbed H\textsubscript{2}O molecules (\(v_2\)) can be identified. We find that \(v_1=459\) meV and \(v_2=436\) meV for ZrO\textsubscript{2} and \(v_1=453\) meV and \(v_2=432\) meV for Nd\textsubscript{0.1}Zr\textsubscript{0.9}O\textsubscript{1.95}. The different frequencies reflect the dynamics of surface O and H atoms to underlying local structure in pure ZrO\textsubscript{2} and Nd\textsubscript{0.1}Zr\textsubscript{0.9}O\textsubscript{1.95}. As the
water content increased, the $\nu_2$-band became broader and shifts to slightly low energies, approaching to that of bulk water.

4 Summary

We present a study of atomic dynamics in the bulk and interfacial region of nano-structured powders of pure and lanthanide-modified zirconia. The long-wavelength optical phonons and the phonon densities of states were characterized by Raman and neutron scattering, respectively. The phonon DOS of $\text{ZrO}_2$, $\text{Ce}_{0.1}\text{Zr}_{0.9}\text{O}_2$ and $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$ exhibits a narrow band in the 20-50 meV and a broad band extend to about 100 meV. Salient features corresponding to the different global crystal and local structures among these powders were observed in the oxygen phonons in the 50-120 meV region. The dynamics of adsorbed hydroxyl groups and water in these powders are also studied by neutron inelastic scattering. It appears that neutron spectroscopy is a useful tool for the study of structure and atomic dynamics of nano-structured materials.
REFERENCES

[10] The energy units of meV and cm⁻¹ are related by 1meV=0.8066cm⁻¹.
Figure captions

Fig 1 Raman scattering spectra for pure ZrO$_2$, heated at (a)290°C, (b)600°C and (c)1000°C.

Fig 2 Raman scattering spectra for Zr$_{0.9}$La$_{0.1}$O$_{1.95}$, heated at (a)600°C, (b)800°C and (c)1000°C.

Fig 3 The phonon densities of states for pure ZrO$_2$, Ce$_{0.1}$Zr$_{0.9}$O$_2$, and Zr$_{0.9}$Nd$_{0.1}$O$_{1.95}$. The powders were heat-treated at 600°C. The Raman frequencies of the phonons (pure monoclinic ZrO$_2$) are denoted by arrows.

Fig 4 The O-H stretch vibration bands observed in ZrO$_2$ and Zr$_{0.9}$Nd$_{0.1}$O$_{1.95}$ by neutron scattering with an incident energy of 600 meV. The components for chemisorbed OH group and physisorbed H$_2$O are represented by dotted and dashed lines, respectively.
Fig 1

Raman shift (1/cm)

Intensity (a.u.)
Fig 2
HRMECS
$E_0 = 150 \text{ meV, 7 K}$

Generalized Phonon DOS (arb. units)

$\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$
$\text{Ce}_{0.1}\text{Zr}_{0.9}\text{O}_2$
$\text{ZrO}_2$

$E$ (meV)
Fig. 4.

HRMECS
600 meV
25 K

Nd$_{0.1}$Zr$_{0.9}$O$_{1.95}$

ZrO$_2$

$S$ (arb. units)

3226 4033 (cm$^{-1}$)

350 400 450 500 550

E (meV)
HRMECS
$E_0 = 150$ meV, 7 K

Nd$_{0.1}$Zr$_{0.9}$O$_{1.95}$
Ce$_{0.1}$Zr$_{0.9}$O$_2$
ZrO$_2$

Generalized Phonon DOS (arb. units)

E (meV)
\[ E \text{ (meV)} \]

Graph showing data for ZrO\(_2\).
HRMECS
600 meV
25 K

Nd_{0.1}Zr_{0.9}O_{1.95}