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lanthanide-modified zirconia nanoparticles***

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Dynamic Response of Physisorbed Hydrogen Molecules on Lanthanide-Modified Zirconia Nanoparticles

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Ultrafine lanthanide ($\text{Ln} = \text{Ce}$ and Nd)-modified zirconia powders synthesized by a coprecipitation method exhibit high surface areas and heterogeneous adsorption sites that are essential for catalytic applications. We report a study of the surface chemistry of $\text{Ce}_{0.1}\text{Zr}_{0.9}\text{O}_2$ and $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$ powders. First, the specific surface area and porosity are characterized by nitrogen isotherm-adsorption measurements. Second, the motion of hydrogen molecules physisorbed on Ce- and Nd-doped zirconias is studied by inelastic neutron scattering. Nitrogen adsorption-desorption isotherm measurements yield a BET surface area ($26.1 \text{ m}^2/\text{g}$) and mesopore size ($\sim 5 \text{ nm}$ radius) in $\text{Ce}_{0.1}\text{Zr}_{0.9}\text{O}_2$ as compared to those ($72.3 \text{ m}^2/\text{g}$ and $\sim 3 \text{ nm}$) in $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$. The vibrational densities of states of H_2 on $\text{Ce}_{0.1}\text{Zr}_{0.9}\text{O}_2$ and $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$ were measured at 20 K over the $0\text{--}200 \text{ meV}$ energy range for three hydrogen coverage. The spectra for both samples consist of two parts: a sharp peak at $\sim 14.5 \text{ meV}$ and a broad component extending beyond 200 meV . The sharp peak corresponds to transitions from the $J=0$ to $J=1$ rotational states of bulk hydrogen molecules, and its intensity decreases with decreasing H_2 coverage. The broad component corresponds to overdamped motion of surface adsorbed hydrogen molecules. The major difference in the latter component between the Ce- and Nd-doped samples is an excess of intensities in the $5\text{--}14 \text{ meV}$ region in $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$. The confined motion of adsorbed H_2 on the different micropore and mesopore surfaces of $\text{Ce}_{0.1}\text{Zr}_{0.9}\text{O}_2$ and $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$ is discussed.

1. Introduction

High-surface-area zirconias are widely used as catalytic support of noble metals or oxygen sensor electrolyte in automobile exhaust-emission-control systems. Doping zirconia with small amount of lanthanide elements (Ln) may tailor its properties for better catalytic performance. Our studies of Ln-ZrO₂ systems are motivated by the need for better support materials for noble metals in three-way catalytic converters for automobiles. First, the thermal stability of the materials is of interest. Ln-doping helps stabilize the cubic and tetragonal phases over a wide range of temperatures thereby removing the disruptive phase transformations in pure zirconia. Second, it is important to preserve the high surface area and activity of heterogeneous adsorption sites at elevated temperatures. Substituting Zr⁴⁺ ions with trivalent Ln cations such as Nd³⁺ gives rise to oxygen vacancies and adsorption of (OH)⁻ ions in the lattice as a result of charge compensation. As Ce is known to undergo valence changes under redox conditions, Ce-modified zirconia may provide added oxygen storage capability in promoting oxidation reaction of carbon monoxide and hydrocarbons as well as deoxidation reaction of nitric oxide during a catalytic cycle. Finally, modification of interfacial energies, oxygen diffusion coefficients, crystalline anisotropy and other properties should be characterized systematically according to the dopant elements, preparation methods and processing routes. Clearly, a comprehension of these phenomena requires coordinated investigations employing many different techniques.

In the case of Ce_{0.1}Zr_{0.9}O₂ and Nd_{0.1}Zr_{0.9}O_{1.95} which are synthesized by a coprecipitation method starting from aqueous solutions of ZrOCl₂ and LnCl₃, we have applied neutron spectroscopic methods to study the crystal-phase morphology [1], microstructure [2], phonon density of states [3], and proton dynamics of adsorbed OH groups and water [1]. The crystal structure was found to be of tetragonal symmetry and of mixed cubic + tetragonal phases for Ce_{0.1}Zr_{0.9}O₂ and Nd_{0.1}Zr_{0.9}O_{1.95}, respectively. Depending on the drying and heat treatments, aggregates of secondary particles comprised of nanoscale crystalline grains may lead to fractal-like microstructure. Here we present the results of a study of the porosity and surface

chemistry of these fine powders by nitrogen-adsorption isotherm measurements and inelastic neutron scattering from physisorbed hydrogen molecules.

2. Experimental details

The 10 mol% Ln-modified zirconia (Ln = Nd and Ce) powders were prepared by a coprecipitation technique. Mixtures of hydrous zirconium and lanthanides were coprecipitated from an agitated aqueous solution of ZrOCl_2 and LnCl_3 (total concentration of 0.8 mol^{-1} at the final pH value of 10) with excess of 10 wt.% NH_4OH solution. The products were filtered and washed with distilled water, and then dried by a supercritical technique. The dried mixtures were calcined at 600°C in air for 3 h. Details concerning the preparation and characterization of the Ln-modified zirconias have been given previously elsewhere [4].

The adsorption-desorption isotherms of nitrogen at 77 K measured with the apparatus Autosorb (Quantachrome, USA) as a function of relative pressure P/P_0 over the range of 0.01-0.99. Prior to the a measurement, the sample was outgassed at $\sim 150^\circ \text{C}$ under vacuum for 8 h. Pore volume was estimated from nitrogen uptake at $P/P_0 \approx 0.99$.

The neutron scattering experiment was performed using the QENS spectrometer at the Intense Pulsed Neutron Source (IPNS) of Argonne National Laboratory. The energy resolution of the QENS spectrometer corresponding to the present sample configurations varies smoothly from about 0.12 meV at the elastic position to $\sim 2.2 \text{ meV}$ at an energy transfer of 50 meV. After outgassing the powder, hydrogen gas was introduced to about 20 g of powder inside a cylindrical cell as the sample is cooled from room temperature to $\sim 20 \text{ K}$ by a closed-cycle helium refrigerator. All neutron measurements were conducted at 20 K. Data were collected for both powders at three H_2 dosages, approximately 5.6×10^{-4} , 2.9×10^{-4} , and 0.64×10^{-4} mole per gram of sample. The data were corrected for background scattering from the undosed sample and container by subtracting the data of a corresponding run with no hydrogen. Each data set

consists of three spectra of scattered intensities recorded by three detector banks covering different ranges of neutron momentum transfers.

3. Results and discussion

3.1 Nitrogen adsorption-desorption isotherms

The isotherms of both $\text{Ce}_{0.1}\text{Zr}_{0.9}\text{O}_2$ and $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$ exhibit a shape of Type IV with a Type A hysteresis loop [5, 6], as shown in Fig. 1. This is characteristic of mesoporosity with principally open-ended cylindrical pores. The hysteresis loop of $\text{Ce}_{0.1}\text{Zr}_{0.9}\text{O}_2$ occurs at higher relative pressures than those of $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$, which is indicative of a larger average pore radius. A BET and t-plot analysis confirmed that the specific surface area, pore volume and pore radius are 26.1 m^2/g , 0.130 cc/g and 5 nm for $\text{Ce}_{0.1}\text{Zr}_{0.9}\text{O}_2$; and 72.3 m^2/g , 0.163 cc/g , and 3 nm for $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$. The uptake of adsorption at a characteristic relative pressure (~ 0.6 and ~ 0.75 for $\text{Ce}_{0.1}\text{Zr}_{0.9}\text{O}_2$ and $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$, respectively) in the isotherms signifies multilayer condensation of hydrogen in the mesopores. At low pressure, the isotherms display the characteristic of monolayer adsorption on micropores (pore radius small than ~ 2 nm). This behavior is common to zirconia powders prepared using aqueous solutions and subsequently dried at a low temperature. [7, 8] The powders usually consist of micropores which are formed between tightly bound nanocrystalline grains, as well as mesopores which are present within aggregates of secondary particles.

3.2 Neutron scattering from physisorbed hydrogen

The motion of hydrogen molecules physically adsorbed on a solid surface is sensitive to the potential modulation over the surface and the temperature. Under certain energetic configurations hydrogen molecules may diffusive from one adsorption site to another, undergo localized vibrations and/or rotations defined by a potential minimum at a fixed site, or interact with other particles. Since hydrogen features a large neutron incoherent scattering cross section, it is often used as a convenient and effective probe in neutron spectroscopic studies of surfaces

properties of porous materials. Fig. 2 shows the excitation spectra of 2.9×10^{-4} mol/g of hydrogen dosage for the $\text{Ce}_{0.1}\text{Zr}_{0.9}\text{O}_2$ and $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$ powders at low and high momentum transfers. The spectra in general exhibit a rise of intensity from about 1 meV to a broad maximum around 25 meV and then an extension to higher energies beyond 100 meV. In addition, a sharp peak at approximately 14.5 meV is clearly evident in $\text{Ce}_{0.1}\text{Zr}_{0.9}\text{O}_2$ (Fig. 2a), and it becomes weaker in Fig. 2b. The position of this peak and the momentum-transfer dependence of its intensity are consistent with the well-know transition of the $J=0$ to $J=1$ rotational states of bulk hydrogen molecules. [9] This transition is absent or very weak in $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$. The broad component of the spectra has an opposite momentum-transfer dependence of intensity, namely, it is more intense at higher momentum transfer. This is characteristic of phonon or molecular vibrational density of states of the adsorbed hydrogen. Furthermore, $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$ exhibits a higher phonon density in the 5-14 meV region as compared to $\text{Ce}_{0.1}\text{Zr}_{0.9}\text{O}_2$.

We also measured the excitation spectra at different coverage of hydrogen. At a high coverage of 5.6×10^{-4} mol/g, besides an increase of overall intensities for both powders, a sharp rotational ($0 \rightarrow 1$) transition appeared also in $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$. At a low coverage of 0.64×10^{-4} mol/g, the shape of the spectra is similar to those in Fig.2 but the count rate and statistics are much lower as expected from the reduction of hydrogen dosage.

We interpret the broad component of the spectra in both powders as the phonon/molecular vibrations density of states of surface adsorbed hydrogen. N_2 -adsorption isotherm and neutron small-angle scattering results indicate that the powders comprise micro- and mesoporous surfaces with pore size distribution spreading from 1 to 100 nm. Moreover, the aggregates can be described as mass fractals with fractal dimension of 1.9 and 2.9 for $\text{Ce}_{0.1}\text{Zr}_{0.9}\text{O}_2$ and $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$, respectively. [2] Therefore, the modulation of the surface potential is expected to be very irregular. The hydrogen molecules is likely to undergo

overdamped motion through inter-particle relaxations and energy transfer processes. The excitation spectrum is broad and diffuse over a wide range of energies. The different phonon densities in the 5-14 meV region between $\text{Ce}_{0.1}\text{Zr}_{0.9}\text{O}_2$ and $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$ probably reflect a somewhat dissimilar microporosity in the two powders. As $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$ contains crystalline grains of mixed cubic and tetragonal structure whereas $\text{Ce}_{0.1}\text{Zr}_{0.9}\text{O}_2$ contains a single tetragonal phase, the microporosity is expected to be more heterogeneous for $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$. On the other hand, since $\text{Ce}_{0.1}\text{Zr}_{0.9}\text{O}_2$ has a surface area about 3 times smaller than $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$, multilayer hydrogen condensation within the mesopores will occur in $\text{Ce}_{0.1}\text{Zr}_{0.9}\text{O}_2$ at a lower dosage. This explains the appearance of the 0 \rightarrow 1 transition of bulk-hydrogen rotation at a 2.9×10^{-4} mol/g coverage in $\text{Ce}_{0.1}\text{Zr}_{0.9}\text{O}_2$ but not in $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$.

4. Summary

We investigated the microstructure and surface properties of ultrafine Ce- and Nd-modified zirconia powders by a joint adsorption-isotherm and neutron-scattering study. While the average pore size distribution and specific surface area can be determined by an BET analysis of nitrogen adsorption, neutron inelastic scattering from surface adsorbed hydrogen provides additional information about the modulation of local potential energies over the substrate surfaces and distinguishes subtle differences in the microporous and mesoporous structure of the two samples.

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Figure Captions:

Fig. 1 Nitrogen adsorption-desorption isotherms at 77 K for $\text{Ce}_{0.1}\text{Zr}_{0.9}\text{O}_2$ and $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$.

Fig. 2 The excitation spectra of 2.9×10^{-4} mole of hydrogen gas adsorbed per gram of sample on $\text{Ce}_{0.1}\text{Zr}_{0.9}\text{O}_2$ and $\text{Nd}_{0.1}\text{Zr}_{0.9}\text{O}_{1.95}$ powders measured at 15 K by the low momentum-transfer (a) and high momentum-transfer (b) detector banks of the QENS spectrometer.



