Catalyst Materials for High-Temperature Processes
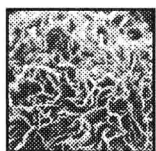
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Preface

"Catalyst Materials for High Temperature Processes" is a collection of fifteen, peer-reviewed, cross-cutting interdisciplinary papers in this growing, industrial important field of catalysis. The papers are based on oral and poster presentations given at the 1996 Annual Meeting and Exposition of The American Ceramic Society held April 14–17, 1996, in Indianapolis, Indiana. The papers have an international flavor representing insight and perspective from prominent researchers and technologists throughout the world.

Looking toward the future, new and improved catalytic materials that can meet and sustain stringent performance criteria will play an important role in meeting the needs for cleaner and more efficient machines, processes, and industries. Equally important is the need for more efficient use of our limited natural resources.

There are a number of catalyst applications that stand to benefit from operation at temperatures. Some important industrial applications for high-temperature catalysts include NO_x, CO, SO_x, hydrocarbon and particulate control from fossil-fueled (both gasoline and diesel) internal combustion engines; destruction of volatile organic chemicals (VOC); catalytic combustors including high-temperature gas turbines; high-temperature fuel cells; and steam-hydrocarbon reforming for producing hydrogen and synthesis gas.

The benefits of working at high temperatures include higher reaction rates, throughput, energy efficiency, and heat recovery. The problems inherent with high temperature align with the material's ability to maintain integrity and sustain performance due to loss of active surface area through sintering, phase change, formation of new phases, and component volatility. The collection of papers is a mix of applied science and technology applications of high-temperature catalysts. The applied science seeks to understand the physical and chemical phenomena that can lead to improved catalyst performance. Backstopped by powerful instrumental research tools, these studies are unraveling molecular and atomistic-level insight and understanding of composition-structure-property-reactivity relationships of materials—the properties that determine the catalyst performance. Technology applications for high-temperature catalytic materials that are covered in the papers include methane reforming, automotive and diesel exhaust catalysts, catalytic combustion for gas turbines, and membranes.

I want to thank all who made the symposium possible, and in particular Dr. Zenfir Ismagilov of Institute of Catalysis, Novosibrisk, Russia, for inspiring me to organize this syposium and to Drs. Richard M. Spriggs (Alfred University) and Rasto Brezny (W.R. Grace Inc.) for their unflinching assistance in organizing the various sessions.

K.S. Ramesh

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ADVANCES IN AUTOEXHAUST CATALYSTS

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INTRODUCTION

Exhaust emission standards were set by the Clean Air Act Amendments of 1970 requiring automobile manufacturers to control the amount of hydrocarbons (HC), carbon monoxide (CO) and oxides of nitrogen (NO_x) emitted from vehicles. These emissions from vehicles have been significantly reduced in the 20 years since auto exhaust catalysts was first used. Non-methane hydrocarbons and NO_x emissions from vehicles, which are the root causes of photochemical smog, come under more stringent control year by year. Hydrocarbon emissions are required to be reduced to less than one-fifth of their present levels by the year 2000.[1]

To meet this stringent hydrocarbon emission standards, one of the cold start strategies is to use a quick light-off catalyst which is mounted at a close-coupled manifold position.[2)-4)] In this application, it is inevitable that current TWC catalysts is thermally deactivated, because the catalyst is exposed to high temperatures, 100-150°C higher than the catalyst would encounter at the underfloor position. Our future catalyst development has focused on minimizing thermal deactivation via stabilization of ceria (CeO_2), which is used as an oxygen storage component (OSC) in TWC catalysis.

This paper summarizes the fundamental characteristics of CeO_2 as the OSC and

introduces our new technology for maximizing CeO_2 function even under high temperature conditions.

EXPERIMENTS

Sample and Catalyst Preparation

A commercially available bulk CeO_2 was used in the experiments. CeO_2 stabilization were carried out by impregnation with promoter solutions, followed by calcination at 500 °C. Pt, Rh and Pd were added to these materials by impregnation to 1 wt% precious metal. Thermal treatments were conducted in air between 500-1,000 °C in an electric furnace. The catalysts used were Pt/Rh=5/1, 1.6 g/liter, with 47 cells/cm^2 monolithic substrates, with washcoat containing proprietary stabilizers and the OSC materials.

Characterization

Adsorption characteristics were evaluated by a TPR method using 5% H_2/Ar stream with a rate of 50 ml/min flow and a 10 °C/min programmed temperature ramp. O_2 uptake was measured by an O_2 pulse method at 500 °C in a He atmosphere. Pretreatment of the samples was conducted at 500 °C for 10 min in a 5 % H_2/Ar stream before introduction of the O_2 pulse.[5] BET surface area was measured by a one point N_2 adsorption method. Pt and CeO_2 crystallite size were measured by an XRD method.

Catalyst Evaluation

To accelerate the catalyst deactivation modes, the catalysts were aged on an engine dynamometer using a 950 °C lean A/F test cycle for 100 hr. TWC catalytic performances were evaluated using lambda sweep tests at 400 °C and 500 °C.[5]

CHARACTERISTICS OF CeO_2

CeO₂ Redox Chemistry

Chemical reactions near the stoichiometric air to fuel ratio conditions where CO, HC and NO_x are simultaneously purified over current TWC catalysts involve redox chemistry. An oxygen storage component is added to the TWC catalysts as a promoter in order to diminish the influence of the air to fuel ratio (A/F) variations on catalytic performance. CeO_2 is usually used as the OSC.

CeO_2 is a non-stoichiometric compound.[6-7] CeO_2 exhibits two valences, Ce^{3+} and Ce^{4+}, and stores and releases oxygen easily, as shown in the following equation.

$$CeO_2 \underset{\text{Oxidation}}{\overset{\text{Reduction}}{\rightleftharpoons}} CeO_{2-x} + (x/2)O_2$$

The ionization energy from Ce^{3+} to Ce^{4+} is so low that CeO_2 functions as an OSC without a change in the crystallite structure. Hence, the addition of CeO_2 to the TWC catalyst results in a significant enhancement of catalytic activity in the operating A/F window by dampening the A/F variations .
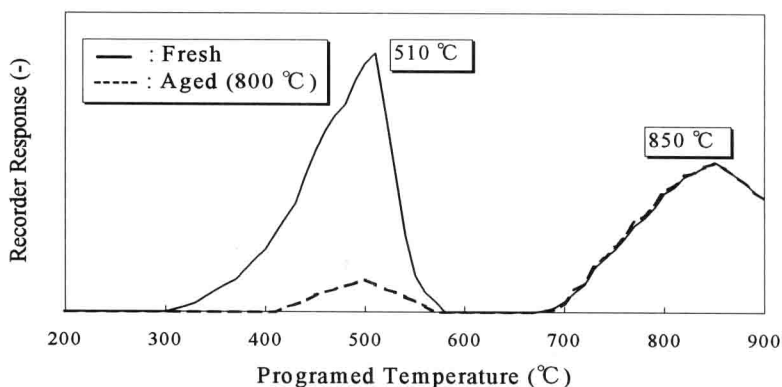

Figure 1   TPR spectra of bulk CeO_2.

Adsorption Characteristics of CeO$_2$

Figure 1 shows the TPR spectrum of bulk CeO$_2$. The reduction peak around 500 ℃ is surface capping oxygen (SCO), and the peak above 850 ℃ is bulk oxygen.[6] These are diagnostic for the formation of low valent CeO$_{2-x}$. Thermal aging of CeO$_2$ resulted in a significant decrease in the SCO, but caused no change in the bulk oxygen. This suggests that non-stoichiometric Ce^{3+} oxide associated with an O$_2$ lattice defect in the CeO$_2$ changes to the thermodynamically stable Ce^{4+} oxide on thermal aging. Since the operating temperature ranges for auto exhaust catalysts are 250-600 ℃, only the SCO can contribute to catalytic reactions.

Figure 2 summarizes the thermal aging profile of CeO$_2$ as measured by O$_2$ uptake at 500 ℃ using an O$_2$ pulse method. The uptake of O$_2$ by CeO$_2$ depends strongly on the aging temperature. It decreases to less than one-tenth that of a fresh sample after thermal aging above 800 ℃. Alternative treatments by hydrogen and oxygen at 500 ℃ were made with no change in O$_2$ pick up, suggesting the residual SCO can still contribute to the catalytic reactions after high temperature exposure .
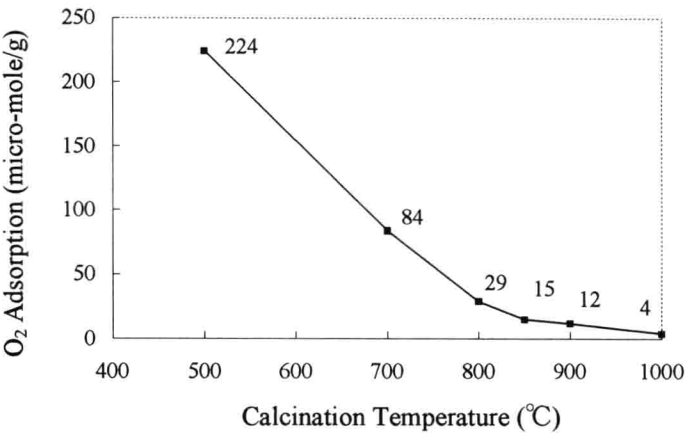
Figure 2   Effect of calcination temperature on O$_2$ adsorption of bulk CeO$_2$.
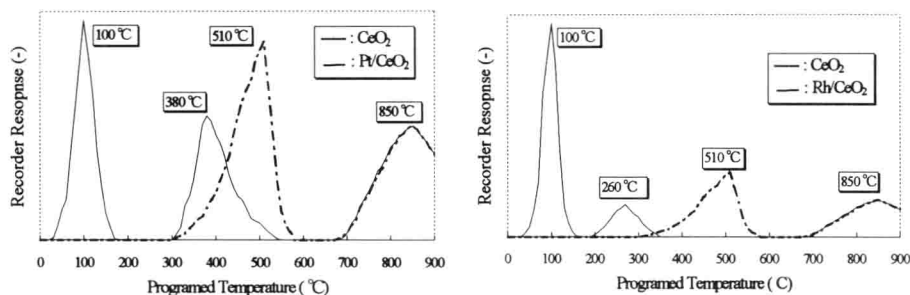
Figure 3   TPR spectra of Pt/CeO₂ and Rh/CeO₂.

Precious Metal - CeO₂ Synergism

Figure 3 shows the TPR spectra of Pt/CeO₂ and Rh/CeO₂. The bulk oxygen of CeO₂ was not activated even when Pt was present. The spilled-over hydrogen can apparently react with only the SCO at a lattice defect of the CeO₂. The SCO of the Rh are reduced at around 100 °C, and the SCO on the CeO₂ are activated for reduction at around 280 °C, which is lower than that of the Pt induced change. This difference may be caused by differing activation energies of the SCO on the CeO₂ or rates of hydrogen spill over .

Figure 4   Effect of PM species on reversible SCO of CeO₂ after 1000 °C calcination.

Figure 4 shows the effects of precious metal species on the reversible SCO of the CeO₂. The SCO on the CeO₂-only sample decreases significantly after thermal aging at 1,000 °C, whereas those of CeO₂ in intimate contact with the precious metal are maintained. The ranking of the precious metal effectiveness on the SCO maintenance after thermal aging is Rh, Pd and Pt.
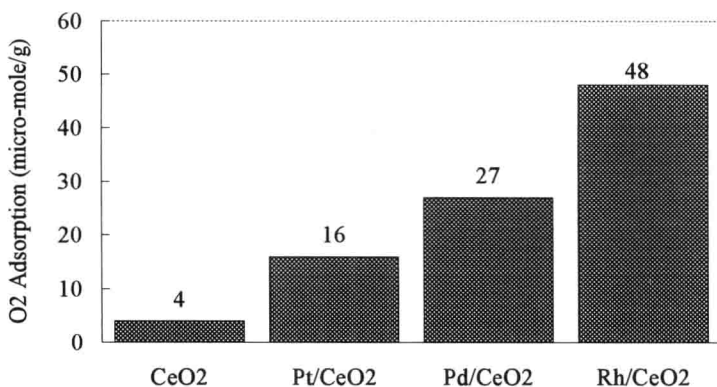
THERMAL DEACTIVATION OF CeO₂ AND IMPROVEMENT

Catalyst Thermal Deactivation

Figure 5 shows the change in: 1) Pt crystallite size, 2) CeO₂ crystallite size and 3) O₂ adsorption of the catalysts that underwent engine aging. Pt metal crystallite size was relatively stable up to 800 °C, and then sintering occurred. CeO₂ crystallite size was directly proportional to the aging temperatures. The O₂ adsorption rapidly decreased at aging temperatures above 800 °C. O₂ storage capacity decreased as the Pt metal sintered and the CeO₂ crystallized. Hence, the major causes of Pt/Rh/CeO₂ TWC catalyst thermal deactivation is Pt metal sintering and decreased O₂ storage capacity resulting from CeO₂ crystallization.
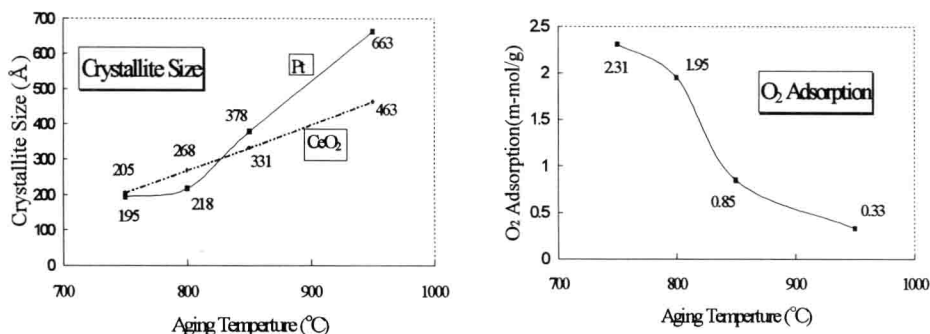
Suppression of CeO₂ Crystallization

Figure 5   Pt and CeO₂ crystallite size and O₂ adsorption of Pt/Rh/CeO₂ catalyst.
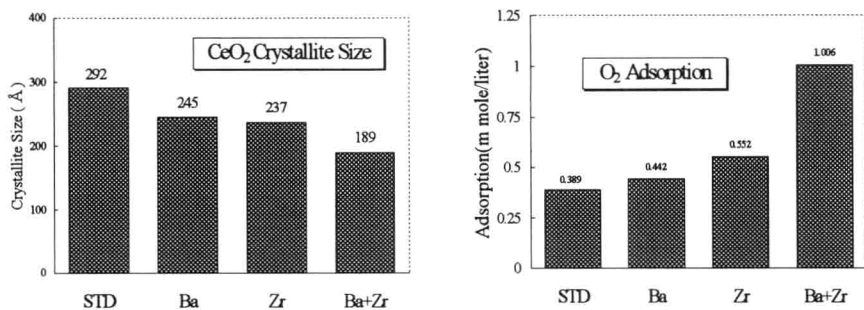
Figure 6   Effect of promoters on CeO₂ crystallization and O₂ adsorption.

One strategy to minimize thermal deactivation of the catalyst is to suppress CeO_2 crystallization by adding promoters. Figure 6 shows the effects of the promoters, Ba and Zr, on both CeO_2 crystallite size and O_2 adsorption in Pt/Rh/CeO_2 catalysts that were thermally aged in air for 10 hr at 900 ℃. The smaller the CeO_2 crystallite size, the higher O_2 adsorption. Although Ba and Zr alone inhibited the CeO_2 crystallite size growth and O_2 adsorption was retained, the combined effects of Ba and Zr were found to be more effective. It was assumed that a part of the CeO_2 reacts with Ba or Zr, and forms Ce/Ba or Ce/Zr mixed oxides or solid solution. These would have been resulted in moderation of CeO_2 crystallization. However, an XRD analysis did not show the presence of these mixed oxides because of only small quantities of the promoters contained in the catalyst. These effects were confirmed under engine aging conditions.

Catalytic Activity Improvement

Table I shows conversion efficiencies of Pt/Rh/CeO_2 TWC catalysts and their respective changes in physical properties after 950 ℃ lean engine aging. In comparison with the standard, the sample with Ba and Zr showed a 2-19 % higher conversion efficiency. Although the presence of Ba or Zr in the catalyst formulation benefited the performance versus the standard catalyst, the combined effects of Ba

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	Conversion(%)						Crystal Size		
	400℃			500℃					
Catalyst	CO	HC	NO	CO	HC	NO	CeO₂	Pt	O₂ Adsorption
STD	48	58	62	63	75	64	453	672	0.39
Ba	55	65	64	74	77	69	292	639	1.45
Zr	49	63	61	71	77	66	315	680	1.09
Ba+Zr	58	67	64	82	80	73	246	645	1.84

CeO₂/Pt: Crystallite Size（Å）   O₂ Adsorption : m mole/liter-catalyst at 400℃

and Zr were obviously more effective. CeO_2 crystallite size and O_2 adsorption of the catalysts were found to be proportional to the conversion efficiency. The smaller CeO_2 crystallite size and the higher O_2 adsorption resulted in higher conversion efficiencies.

NEW THERMALLY STABILIZED OSC

Role of Ba and Zr in CeO_2 Containing TWC Catalyst

As mentioned above, the addition of Ba and Zr to the CeO_2 containing TWC catalysts were found effective to improve CeO_2 thermal stability. In order to identify each role, the effects of Ba and Zr addition to CeO_2/Al_2O_3 and CeO_2 were investigated separately. Figure 7 summarizes the BET surface area of each sample aged in air at 800-1100 ℃. For the CeO_2/Al_2O_3 system, both samples showed higher BET surface area than the sample without addition after 900 ℃ aging. However, the Ba containing sample showed the highest BET surface area after 1100 ℃ aging. These results suggest that the effect of Ba is more important than Zr in Al_2O_3 stabilization.
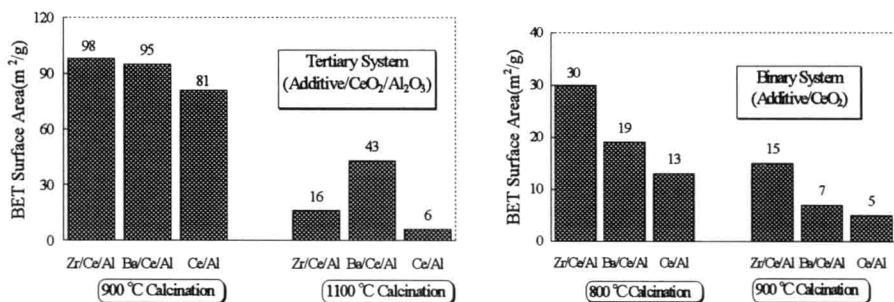
Figure 8   Effect of Zr and Ba addition on CeO_2/Al_2O_3 and CeO_2-only stabilization.

For CeO_2, the Zr containing sample shows the highest BET surface area after aging at 800 °C and 900 °C. This suggests that Zr is clearly more effective in CeO_2 stabilization than Ba. The ionic radius of Ce^{4+}, Ce^{3+}, Zr^{4+} and Ba^{2+} are 0.95Å, 1.03Å, 0.80Å and 1.38Å, respectively. It is assumed that Zr is easily introduced into the lattice of CeO_2 to form Ce/Zr solid solution to suppress CeO_2 crystallization. Because ionic radius of Zr is smaller than that of Ce^{4+}. Ba would be supported on CeO_2 because of its larger ionic radius than Ce.
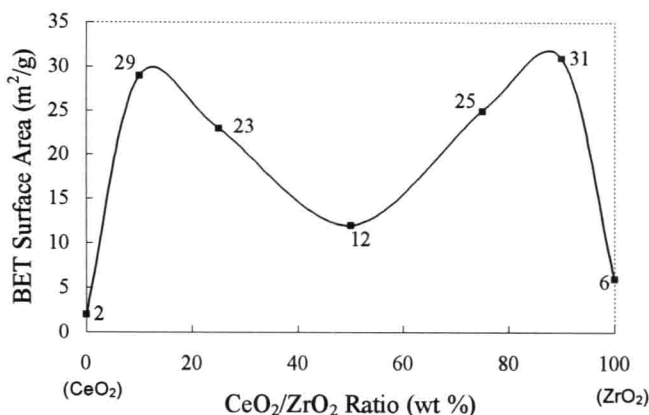

Figure 8   Effect of CeO_2/ZrO_2 weight ratio on BET surface area.

Ce/Zr Multiple Oxides

To investigate the formation of a Ce/Zr solid solution or multiple oxides, Zr/Ce compounds with different Zr/Ce weight ratios were prepared and evaluated. Figure 8 shows the BET surface area of those compounds. Their BET surface areas are higher than that of pure bulk CeO_2 or ZrO_2 after 900 ℃ aging in air. 10% Zr/CeO_2 and 10% Ce/ZrO_2 showed the highest BET surface areas. In the case of 10% Zr/CeO_2, Zr would form multiple oxides with CeO_2. However, for 10% Ce/ZrO_2, Ce would be dispersed on ZrO_2 or form multiple oxides with ZrO_2, due to larger ionic radius than ZrO_2.
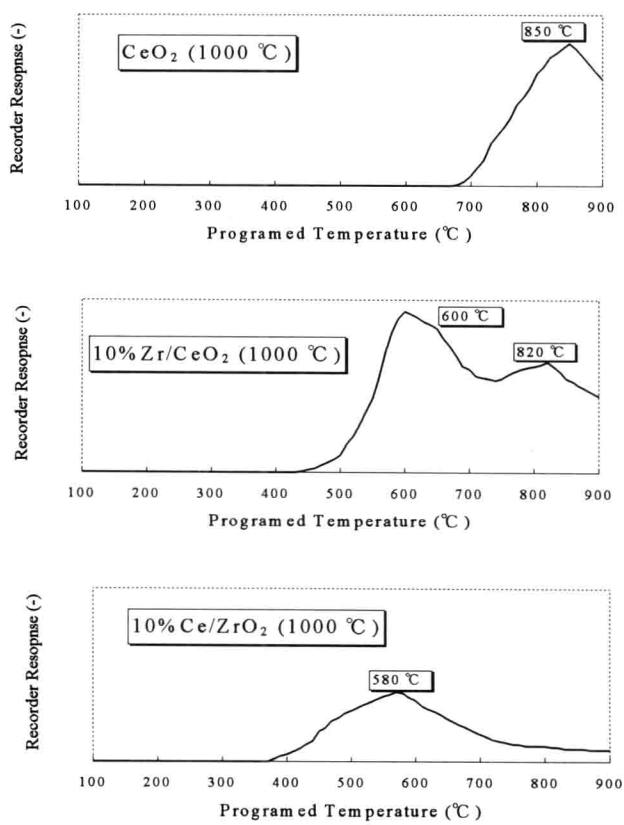

Figure 9　Comparison of TPR spectra among CeO_2, 10%Zr/CeO_2 and 10%Ce/ZrO_2.

Catalyst Materials for High-Temperature Processes