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Role of cerium–zirconium mixed oxides as catalysts for car pollution: A short review[1]

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Abstract

This article focuses on the role of mixed oxides in the Ce–Zr–O system, which is important as an excellent promoter for oxygen storage capacity in automotive three-way catalysts. In a model of Pt–alumina catalysts, there is a clear effect of CeO_2–ZrO_2 solid solution on NO and CO removal activities under dynamic air/fuel conditions. It is suggested that the design and development of automotive catalyst can be realized through research on complex oxides in Ce–Zr–O and related systems. © 1998 Elsevier Science S.A.

Keywords: Automobile exhaust; Catalysis; Ce–Zr mixed oxide

1. Background

The automotive three-way catalyst system (TWC) generally operates under a certain air–fuel ratio (A/F) range. The A/F is controlled by an oxygen sensor device so that the catalyst maintains high purifying activity. Common three-way catalysts consist of precious metals such as Pt, Rh and Pd, promoters and a transition–alumina support. Gandhi and coworkers [1] reported the role of ceria (CeO_2); the addition of CeO_2 promotes dynamic performance in purifying carbon monoxide (CO), nitrogen oxides (NO_x) and hydrocarbons (HC) under conditions of rich–lean A/F in automotive exhaust, which is called the oxygen storage capacity (OSC). CeO_2 provides oxygen for oxidizing CO and HC under rich A/F conditions and removes it from the exhaust gas phase for reducing NO_x under lean A/F. Ce^{4+} in the CeO_2 lattice is readily converted to Ce^{3+} due to its nonstoichiometric behavior [2–4]. The ceria in TWC has several roles including promotion of the water gas shift reaction, the dispersion of precious metals as well as inhibition of the sintering of the alumina support [5–10]. Practical use under thermally harsh conditions resulted in significant degradation of the catalyst, including loss of surface area of the support, sintering of precious metals and deactivation of the ceria. Durability of catalysts is required for the advanced engine systems now being introduced in various new automobile models. Emission regulations have been applied in European countries since 1988, and more rigorous regulations are planned for the USA. This paper is a short review of the role of mixed oxides and possible material aspects of Ce–Zr–O and related systems in industrial rare-earth products for car pollution.

2. Effect of cerium–zirconium mixed oxides on three-way catalysts

Several articles have examined the effect of a zirconium promoter in three-way catalysts, however only a few critical papers deal directly with the OSC of the Ce–Zr–O system in the initial stage of development. Stepien and coworkers studied the effect of a ZrO_2 support for Rh, which had better durability than the Rh–Al_2O_3 system [11]. Funabiki and Yamada described the co-addition of Ce, Zr and Ba to precious metals catalyst [12]. They indicated the formation of several complex oxides in this system which should inhibit sintering of the catalysts. Matsumoto and coworkers argued the role of solid solutions of Ce–Zr–O systems as well as Ce–La–O as OSC promoters in TWC, specifically leading to the improvement of heat durability [13,14]. Masuda and coworkers reported that a ZrO_2 catalyst containing Ce and Pt from the sol–gel method showed lower thermal stability and CO conversion than a Ce–Pt catalyst [15]. Huuska and Maunula examined the effect of Zr, Si, La and Ba on the thermal aging of precious metal catalysts using the TPD technique [16]. Ozawa and coworkers reported the applica-

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tion of Ce–Zr oxide solid solution to three-way catalysts. An excellent improvement in dynamic performance was achieved by the OSC effect of CeO_2–ZrO_2 solid solution formed in Pt/Al_2O_3 and practical catalysts [17].

Here, I summarize several factors for the OSC promoter in the Ce–Zr–O system.

2.1. Inhibition of sintering

The thermal deactivation of TWC is caused by several factors. The main phenomenon is the sintering of the fine particles of precious metals and alumina supports as well as ceria when the catalyst is subjected to exhaust at elevated temperatures for prolonged periods. One recent requirement for materials is thermal stability and durability for hot exhaust at around or above 1000°C. CeO_2 powder readily sinters at elevated temperatures, although it is a good refractory oxide with a high melting point. The addition of zirconium, especially the formation of Ce–Zr mixed oxides, is effective in the inhibition of the sintering of ceria. Simple experiments indicate that Zr modification of CeO_2 powder, followed by solid state reactions, has the effect of improving the thermal stability of CeO_2 promoter [13]. Chemical synthesis processes as well as impregnation are expected to lead to excellent inhibition of the thermal deactivation (sintering) of CeO_2.

2.2. Compounds (phases)

Many researchers have reported the phase diagrams of the CeO_2–ZrO_2 system [18–22]. In the Ce-rich region of the diagrams, a cubic solid solution of $Ce_{1-x}Zr_xO_2$ appears, while tetragonal and monoclinic solid solutions form in the tight regions of the Zr-rich region. In the central region, there are several structures such as tetragonal $Ce_2Zr_3O_{10}$ and other metastable mixed oxides. However, the compounds or mixed oxides of the Ce–Zr–O system are often obtained in their metastable states, which are also useful for catalytic application. It is interesting that the mixed fractions (compositions) of metals in the Ce–Zr–O system form several different kinds of metastable and/or stable solid solutions. In addition, the resulting phases depend on the synthesis route of the oxides. One of the key points for industrial development is the application of these metastable compounds or phases which can be derived by various advanced powder processing technologies.

2.3. Oxygen evolution and nonstochiometry

Oxygen evolution and/or uptake originates from the nonstoichiometry and oxygen diffusion in the surface and lattice of $Ce_{1-x}Zr_xO_2$. The OSC promoter should satisfy two factors: a wide operation range for redox between Ce^{3+} and Ce^{4+} in reducing and oxidizing atmospheres, and a high reaction rate over the modified CeO_2 particles. Fig. 1 shows experimental results for the CO oxidation reaction (in He) with a pulse technique over CeO_2 and modified CeO_2 powders heated at 1000°C. CO is oxidized to CO_2 with active oxygen from the oxide particles. The 0.9 g samples were pre-heated at 800°C for 1 h in flowing oxygen, cooled and then reacted by pulsed CO of 8 μmol at intervals of 3 min in He at a constant heating rate. Solid solutions of $Ce_{0.8}Zr_{0.2}O_2$ are formed in these powders after heat treatment at 1000°C. The results of the pulse reaction indicate excellent improvement of the activity of CeO_2 with the addition of ZrO_2 in both the mixed oxides themselves and alumina-supported oxides.

In situ X-ray diffraction experiments indicate that the steady-state reduction of both CeO_2 and $Ce_{1-x}Zr_xO_2$ powders is described by the simple kinetic equation $kt = \{1-(1-\alpha)^{1/3}\}^2$, where k is the kinetic constant, α a nonstoichiometric parameter for $CeO_{2-\alpha}$, and t the time of reaction in CO/N_2. The reaction was controlled by the diffusion of lattice oxygen to the surface, the same as for Ce–La mixed oxides [23,24]. The formation of Ce–Zr mixed oxides enhances the diffusion rate of lattice oxygen for CO oxidation as well for inhibition of sintering of CeO_2. Such observations of diffusion via aspects of solid state chemistry suggests, in principle, the possibility of more excellent compositions or states existing in the Ce–Zr–O and related systems.

On the other hand, the catalytic reaction for the OSC is the reaction between a reactant such as CO and oxygen at a surface active site of CeO_2. Enhanced oxygen diffusion is an important factor for improving and developing OSC promoters for TWC, however investigation of the pure catalysis of OSC is required for future development. Recently, several researchers have reported a better composition, $Ce_{1-x}Zr_xO_2$, through systematic OSC measurements [25–28].

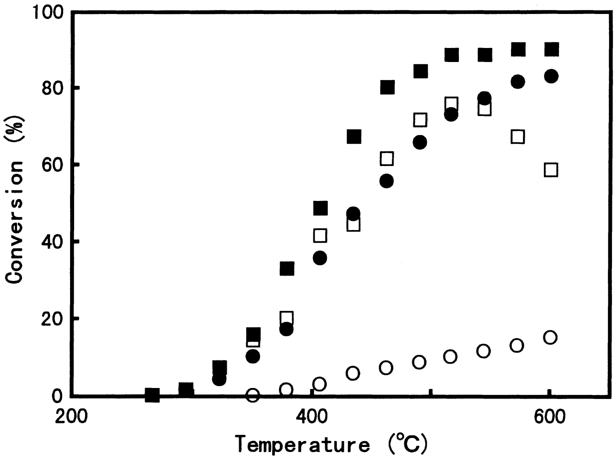

Fig. 1. Conversion (%) to CO_2 for the CO pulse reaction over powders of (○) CeO_2, (●) $Ce_{0.8}Zr_{0.2}O_2$, (□) Al_2O_3-supported CeO_2 (33 wt%), and (■) Al_2O_3-supported $Ce_{0.8}Zr_{0.2}O_2$ (33 wt%). All samples were heated at 1000°C for 3 h in air.

2.4. Dynamic performance of Pt catalysts given by high oxygen storage capacity

Figs. 2 and 3 and Table 1 show examples of the three-way activities of model catalysts: Pt/γ-Al_2O_3, Pt/CeO_2/γ-Al_2O_3 and Pt/$Ce_{0.8}Zr_{0.2}O_2$/γ-Al_2O_3. They were prepared by the physical mixing of γ-Al_2O_3-supported Pt and CeO_2 or Pt and $Ce_{0.8}Zr_{0.2}O_2$. Starting powders of Pt/γ-Al_2O_3, Pt/CeO_2/γ-Al_2O_3 and $Ce_{0.8}Zr_{0.2}O_2$/γ-Al_2O_3 were prepared by the impregnation of aqueous solutions of $Pt(NO_2)_2(NH_3)_2$, $Ce(NO_3)_3$ and a mixture of $Ce(NO_3)$ and $ZrO(NO_3)_2$ with powdered γ-Al_2O_3. Pt/γ-Al_2O_3 was heated at 700°C for 3 h in air, and CeO_2/γ-Al_2O_3 and $Ce_{0.8}Zr_{0.2}O_2$/γ-Al_2O_3 powders were heated at 1000°C for 5 h in air before mixing. The heated samples simulated the degree of sintering in the practical use of Pt-based TWC at high temperatures. XRD measurements of these powders confirmed the formation of crystalline CeO_2 and $Ce_{0.8}Zr_{0.2}O_2$ (solid solution). The three-way activity of the catalysts was tested using a simulated mixture of gases (CO, NO, C_3H_6, CO_2, H_2, H_2O, O_2, N_2 balance) with and without variation of the O_2/CO ratio. The results indicate that the activities of Pt catalysts under conditions of A/F modulation were enhanced by the addition of CeO_2 and much more so by the addition of $Ce_{0.8}Zr_{0.2}O_2$. The activities without modulation were the same regardless of the addition of CeO_2 or $Ce_{0.8}Zr_{0.2}O_2$, because, in this case, the preparation should not influence Pt which is separated physically from CeO_2 and $Ce_{0.8}Zr_{0.2}O_2$. The experiment of the model catalysts shows directly the effect of the mixed oxides themselves on the activities under A/F modulation.

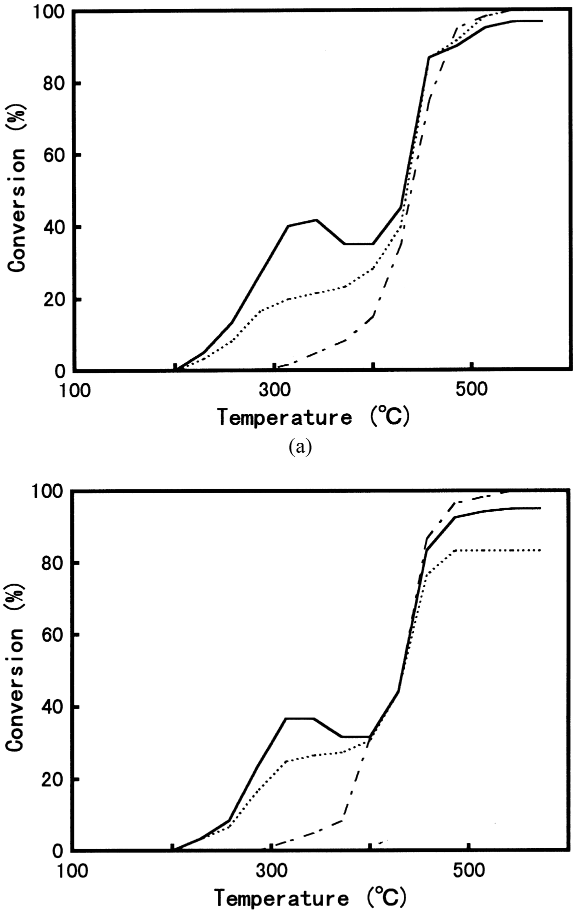

Fig. 2. Three-way removal efficiency vs. temperature for a model exhaust (seven compositions) (a) with and (b) without A/F modulation over Al_2O_3-supported Pt; mixture of powdered (5 wt% Pt/Al_2O_3)$_{0.1}$(Al_2O_3)$_{0.9}$. Conversion of (———) CO, (· · ·) NO, (– · –) HC.

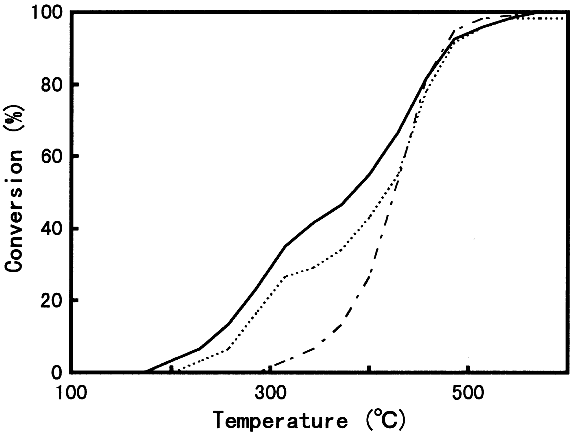

Fig. 3. Three-way removal efficiency vs. temperature for a model exhaust (seven compositions) with A/F modulation over Al_2O_3-supported Pt with CeO_2–ZrO_2; mixture of powdered (5 wt% Pt/Al_2O_3)$_{0.1}$(33 wt% $Ce_{0.8}Zr_{0.2}O_2$/Al_2O_3)$_{0.9}$. Conversion of (———) CO, (· · ·) NO, (– · –) HC.

As matter of fact, the state of the precious metal is very important for designing three-way removal performance. The interaction of precious metals, CeO_2–ZrO_2 and the Al_2O_3 support should be examined with respect to SMSI in oxidizing and reducing atmospheres. There are several studies of ceria and related oxide-supported noble metals promoting the activity of surface oxygen [27–30].

2.5. Thermal durability of the catalyst

Fig. 4 shows the average conversion of CO and NO for two Pt/Rh/Al_2O_3 catalysts using CeO_2 and (Ce,Zr)O_2 [14,31]. They were subjected to high-temperature exhaust at 800–1000°C before catalytic evaluation. Removal efficiencies were measured for a simulated mixture of gases (CO, NO, C_3H_6, CO_2, H_2, H_2O, O_2, N_2 balance). The data indicate that the use of (Ce,Zr)O_2 improves the durability,

Table 1
Removal conversion efficiency (%) of CO, NO and hydrocarbon (HC) for Pt catalysts at 550°C (see text)

Catalyst	CO	NO	HC
Pt/Al_2O_3	95	84	100
Pt/Al_2O_3+Ce/Al_2O_3	97	91	100
Pt/Al_2O_3+Ce–Zr/Al_2O_3	98	99	100

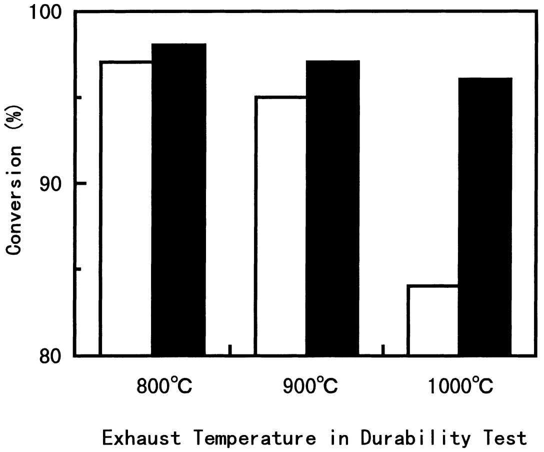

Fig. 4. Average removal efficiency of CO and NO over Pt/Rh/Al_2O_3 catalysts with CeO_2 (☐) and $(Ce,Zr)O_2$ (■) after durability tests using engine exhaust gases at 800, 900 and 1000°C.

specifically the heat-stability, of the catalyst, as well as the initial activity. For practical three-way catalysts with various promoters, it is expected that the durability and performance will be improved by CeO_2–ZrO_2 as OSC promoter without complex rearrangement of other compositions or the catalyst fabrication process.

2.6. Other effects

Other possible roles of Ce–Zr mixed oxides should be investigated, including (a) OSC in low-temperature operation, (b) the water gas shift reaction and other reactions over precious metals supported on CeO_2–ZrO_2, and (c) high dispersion, SMSI and structural features of precious metals on CeO_2–ZrO_2.

3. Mixed oxide products for car pollution

Material–chemical aspects for automotive parts have recently been reviewed by Narula and coworkers [32]. Catalytic materials are important inorganic or ceramic products which are very much in demand, because they are widely used as components in automotive catalytic converters. For example, automotive catalytic heat-stable aluminas must be manufactured using a specialized synthesis method, and are additionally modified in the catalyst fabrication process. Since Ce–Zr mixed oxides and modified CeO_2 promoters have been applied in practice, there is extensive research and development of the oxides themselves as catalytic materials. An inexpensive coprecipitation technique is useful for preparing mixed oxide powders with moderate surface areas in these oxide systems [33,34]. Research using more advanced fabrication techniques should be carried out with the aim of producing fine particles which are highly dispersed and with a surface area as large as the original single and/or mixed oxides. In addition, selection of the Ce/Zr ratio is important for powders and composite materials, as described above [25–28]. Furthermore, third compositions will be expected to improve the OSC of oxides [35–38]. More heat-stable and more OSC-effective compositions should be developed using coprecipitation and modified processes. The phase diagram of CeO_2–ZrO_2–Ce_2O_3 is also useful for describing solid-state redox behavior [39]. Another approach is the examination of structures and the local correlation between atoms in the oxides through advanced characterization methods such as neutron scattering [40]. Of course, detailed studies of catalytic precious metals/oxides system is required [30].

The use of a OSC promoter in TWC is a well-known technology since proposed by Gandhi et al. Recent research reveals that the Ce–Zr–O system and related mixed oxides are more effective than pure CeO_2. In practice, new CeO_2 and/or Ce–Zr mixed oxide powders or other mixed-state materials are expected to be developed as a major group of rare-earth related products. They are essential due to the more stringent exhaust regulations in developed countries, future air pollution standards as well for the economic benefit of automobile-related industries.

4. Summary

This article describes the role of mixed oxides of the Ce–Zr–O system which are important OSC promoters in automotive three-way catalysts. In a model Pt–alumina catalyst, the effect of CeO_2–ZrO_2 solid solution on activity was clearly observed under dynamic A/F conditions. It is suggested that materials research to develop novel OSC promoters of Ce-based complex oxides is required for rare-earth related products for advanced automotive catalysts.

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