In Situ Processing of a Porous Calcium Zirconate/Magnesia Composite with Platinum Nanodispersion and Its Influence on Nitric Oxide Decomposition

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A porous CaZrO₂/MgO composite with $\sim 1\%$ nanodispersed platinum was synthesized in air using several in situ reactions, including the pyrolysis of PtO2. The composite had a uniformly open, three-dimensional pore structure (porosity of 56%), with a narrow pore-size distribution. Catalytic NO decomposition to N₂ and O₂ and NO reduction by C₂H₄ were investigated up to 900°C. In the absence of oxygen, the NO conversion rate reached \sim 52% for the direct decomposition and \sim 100% for the reduction by C₂H₄. The results suggested the possibility of the porous composite as a multifunctional filter for simultaneous filtering of hot gas and removal of NO_x.

I. Introduction

Hor-GAS cleaning is a key issue for various combustion and power applications, for example, in automobiles,¹ advanced biomass-based gasifier engines,² and coal-fueled gas turbines.^{3,4} Porous ceramics are important as the physical filters of soot,^{3–5} as catalysts themselves,^{6,7} and as supports⁸ for the chemical decomposition of toxic species (e.g., NO_x or SO_x).

Recently, the present authors developed uniformly porous $CaZrO_3/MgO$ composites having a three-dimensional network structure.^{9,10} The composites were synthesized using reactive sintering of equimolar dolomite and zirconia mixed powders with LiF additive. During and after the formation of the network structure, CO2 evaporated to form a homogeneous open-porous structure. The pore-size distribution was very narrow (with pore size of $\sim 1 \mu m$), and the porosity was controllable (typically \sim 30%–50%) by changing the sintering temperature.⁹

In this study, we have dispersed nanoscale particles of platinum in a similarly produced CaZrO3/MgO composite and have measured the catalytic activity of NO decomposition and reduction by C_2H_4 .

II. Experimental Procedure

There are several possible routes to disperse nanosized platinum into a ceramic matrix, e.g., electroless plating using a platinum salt,¹¹ metal-organic precursor decomposition,¹² and coating after sintering. In the present work, however, we use the pyrolysis of PtO₂ during in situ processing. PtO₂ can thermally decompose to metallic platinum under ordinary air atmosphere without emission of toxic gas species.

The pyrolysis of a commercial PtO₂ powder (99.9%, Kojundo Chemical Laboratory Co., Ltd., Sakado, Saitama, Japan) was studied using thermogravimetry and differential thermal analysis (TG-DTA) at 10°C/min up to 1200°C in a static air atmosphere. X-ray diffractometry (XRD; CuK_{α} at 40 kV and 100 mA) was used to characterize the PtO₂ powder as well as the composite produced.

High-purity natural CaMg(CO₃)₂ ($<75 \mu m^{13}$), undoped ZrO₂ (99.9%, Sumitomo Cement Co., Tokyo, Japan), PtO₂, and LiF (99.9%, Wako Pure Chemical Industries, Osaka, Japan) powders were used as starting materials: 50:50 (mol%) of CaMg(CO₃)₂ and ZrO2 with PtO2 adjusted to give a composition of CaZrO3/ MgO:Pt = 99:1 (vol%) after sintering. LiF (0.5 wt% of total starting powders) was added to form a liquid phase during sintering to enhance reactivity and neck growth.9 The powders were wet-ball-milled in ethanol for 6 h in a planetary ball-mill (acceleration of 6g). The mixed slurry was dried, subsequently dry-ball-milled for 24 h, and sieved through a 100 mesh screen. The mixed powder was cold isostatically pressed at 200 MPa after mold-pressing. The green compacts (15 mm in diameter and \sim 5 mm in thickness) were sintered in air at 1100°C for 2 h to obtain the porous composite.

The microstructure was characterized using scanning electron microscopy (SEM). The porosity and the pore-size distribution were determined using mercury porosimetry (Model Poresizer 9320, Micromeritics Instrument Corp., Norcross, GA). Mercury intrusion was conducted at pressures between 0 and 207 MPa.

NO decomposition was examined up to 900°C at atmospheric pressure in a quartz microreactor. Gas mixtures of 1000 ppm NO balanced by helium (with or without 500 ppm C_2H_4 as a reducing agent) were passed through the microreactor containing 3 g of the porous CaZrO₃/MgO/Pt composite (containing 141 mg of platinum) at a flow rate of 50 mL/min. NO decomposition was detected using a chemiluminescent NO-NO, analyzer (Model BSU-100uH, Best Instrument, Kyoto, Japan) and was confirmed using gas chromatography (Model CP-2002, Varian Chrompack International, B.V., Middelburg, The Netherlands).

III. Results and Discussion

Figures 1(a) and (b) show the XRD pattern and TG-DTA diagrams of the PtO₂ powder. Figure 1(a) shows the powder consisted of hexagonal α -PtO₂ with some amorphous PtO₂. The color of the as-received PtO2 powder was dark-brown-gray, which suggested the co-existence of dihydrate (PtO₂·2H₂O, brown) and monohydrate (PtO₂·H₂O, black) as well as anhydride (black).¹⁴ Thus, in Fig. 1(b), the first weight loss (and the corresponding endothermic peak) was due to the desorption of the adsorbed water and the dehydration of crystalline water of the dihydrate (i.e., $PtO_2 \cdot 2H_2O \rightarrow PtO_2 \cdot H_2O + H_2O$). The second weight loss (at

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Fig. 1. Characterization of a PtO₂ powder: (a) XRD pattern and (b) TG-DTA diagrams, indicating pyrolysis behavior in air atmosphere.

~100°-620°C) was attributed to the dehydration of crystalline water of the monohydrate as well as the partial decomposition of the dioxide. Platinum has several lower oxidation states.^{15,16} The third significant weight loss and the large endothermic peak were attributed to the pyrolysis of PtO₂. The deoxidation continued at temperatures higher than ~680°C, and it was completed at ~1100°C. The weight loss from 100° to 1150°C was 16.4%, which agreed well with that in the ideal reduction, PtO₂ \rightarrow Pt + O₂. Without distinction of the adsorbed and crystalline water, the

 PtO_2 powder used could be nominally expressed as $PtO_2 \cdot 0.26H_2O$ from the TG-DTA analysis.

Figures 2(a)–(d) show the XRD pattern, pore-size distribution, and SEM micrographs of the porous $CaZrO_3/MgO/1-vol\%-Pt$ composite sintered at 1100°C. XRD analysis revealed that the composite consisted of $CaZrO_3$, MgO, and metallic platinum. The $CaZrO_3/MgO/Pt$ composite (porosity of 56%) had a narrow size distribution with a mean cross section of ~1 µm (Fig. 2(b)) and a well-developed three-dimensional network similar to that of the



Fig. 2. Characterization of the porous $CaZrO_3/MgO/1$ -vol%-Pt composite (porosity of 56%) sintered at 1100°C: (a) XRD pattern, (b) pore-size distribution, (c) SEM photograph (low magnification), and (d) SEM photograph (high magnification).



Fig. 3. NO decomposition activity of the porous CaZrO₃/MgO/1-vol%-Pt composite (porosity of 56%) sintered at 1100°C.

platinum-free composite⁹ (Fig. 2(c)). Fine platinum nanoparticles (~50–100 nm) were observed on the CaZrO₃ and MgO grains (Fig. 2(d)). Such a fine platinum-metal dispersion was attributed to the use of PtO₂ as a starting material, because it could be refined more easily than metallic platinum during the ball-mill processes. The porosity of the *in situ* composites could be controlled by changing the sintering temperature and the CO₂ partial pressure during the sintering.¹⁰

Figure 3 shows the NO decomposition behavior of the porous $CaZrO_3/MgO/Pt$ composite. In the absence of oxygen, NO direct decomposition (filled circle in Fig. 3) reached 52.3% at 900°C. With C_2H_4 as a reducing agent (open circle in Fig. 3), the NO reduction started at ~300°C, and the conversion rate reached 100% at 400°C. However, when only 2% O_2 was present, the NO conversion rate decreased drastically to 3%–4% of that achieved by direct decomposition or NO reduction by C_2H_4 .

Thus, provided that there is not excess O_2 , the porous composite can be applied as a multifunctional filter, i.e., simultaneous hot-gas filtering and NO_x removal in one component. Further studies are required to increase the NO_x removal efficiency and to determine if soots can reduce the catalytic activity or act to remove residual O_2 . It is expected that codispersion with another noble metal using a similar *in situ* process (e.g., nanosized palladium from PdO, or nanosized rhodium from Rh_2O_3) is an effective strategy.

IV. Conclusions

A nanosized-platinum-dispersed CaZrO₃/MgO porous composite with uniformly open pore structure was synthesized. The

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