Hydrothermal Synthesis of New Compounds with the Pyrochlore Structure and Its Application to Nitric Oxide Abatement

Md. Hasan ZAHIR, Kazuyuki MATSUDA, Shingo KATAYAMA and Masanobu AWANO*
Synergy Ceramics Laboratory, FCRA, Shino-Shidami, Moriyama-ku, Nagoya-shi 463-8687
*Synergy Materials Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Shino-Shidami, Moriyama-ku, Nagoya-shi 463-8687

Several new compounds with a pyrochlore-type crystal structure have been synthesized by a low-temperature hydrothermal process under N₂ atmosphere using a mixture of nitrate salts. The chemical compositions of the new pyrochlores are represented as (a) \( Y₂Sn₂CrO₇ \), (b) \( Y₃Mn₂Sn₃CrO₇ \), (c) \( Y₂Zr₂CrO₇ \), (d) \( Ba₆Y₁Sn₇Cr₂O₁₇ \), (e) \( Ba₆Y₁Sn₇Cr₂O₁₇ \), and (f) \( Ca₆Sn₇Ca₃Sn₃O₉ \). The Ba- and Ca-containing pyrochlores exhibited excellent spherical morphology with a pure pyrochlore phase structure and were composed of nanometer-sized particles. A- and B-site-doped pyrochlores maintained a fully ordered crystal structure over a wide temperature range. The pyrochlore oxide powders were tested as catalysts for NO₃ absorption and reduction by CH₄. NO could be almost completely converted into N₂ using hydrothermally derived pyrochlore oxide catalysts in the absence of oxygen at high temperatures. Rapid absorption of NO into alkali-substituted pyrochlores was effective for NO removal from the gas phase, absorption being significantly accelerated by the presence of oxygen.

Key-words: Hydrothermal, Pyrochlore oxide, Morphology, NO reduction, NO₃ absorption

1. Introduction

Hydrothermal synthesis has been known to be a powerful method for the preparation of fine, high-purity and homogeneous powders of various single-component and multi-component oxide powders. Versatility of the pyrochlore materials is mainly associated with their unique crystal structure in which numerous functional substitutions at various lattice sites are possible, producing many compounds with different thermal, electrical, and catalytic properties. However, only a few investigators have attempted to synthesize pyrochlores with two or more different cations at the A site by the hydrothermal process. Several compounds with a pyrochlore structure of \( AA'BB'O₇ \) (\( A=Ca, Sr, Ba, Ph, Cd; A'=La, Pr, Nd, Dy, Ho, Y; B=Ti, Zr, Hf, Sn; B'=Nb, Ta \)) have been synthesized by solid-phase reaction at high temperature. Besides their high energy consumption, these solid-state reactions require a series of laborious heating cycles at high temperatures and repeated grinding of starting oxide components. Thus resulting powders show extensive agglomeration and compositional inhomogeneity.

Two main technologies have emerged recently: the direct reduction of NO by hydrocarbon on stream or by a two-stage operation whereby NO is trapped on a selective sorbent, and then reduced by a short fuel excursion. The key point in the latter strategy is the efficiency of NO absorption materials; they should adsorb (or absorb) a large quantity of NO in a high space velocity gas stream containing both CO₂ and H₂O in the temperature range of 25–350°C. Beliaev et al. first reported the synthesis of mixed pyrochlore oxides with A- and B-site substitution, but the formation of the pyrochlore phase was poor in the case of Ba substitution at A sites. Recently, Hodjati et al. reported that if barium is incorporated in a well-defined structure presenting nanocrystallinity, NO storage is possible with high absorption/desorption capacities. In the literature, numerous authors have claimed that on perovskites, namely, \( LaBO₃ (B=Cr, Mn, Rh) \), NO interacts directly with the surface to form mono or dinitrosyl species or various forms of nitrates. If this perovskite is doped with potassium \( (La₀.₈K₀.₂)MnO₃ \), molecular and dissociative adsorption of NO is observed. Alternatively, if barium is incorporated as the cation at the A-site in the pyrochlore \( AB₂O₄ \), then because of its basicity, one might expect the formation of carbonates and nitrates, particularly in the presence of oxygen.

However, yttrium oxide has been examined as a bulk ceramic for high-temperature applications because of its high melting point, phase stability and low thermal expansion. Moreover, due to the basic nature of yttrium oxide, it has more recently been found to be an effective catalyst for methane dimerization and the selective catalytic reduction of nitrogen oxide. Stannate pyrochlores have attracted much interest for their high efficiency of oxidative coupling of methane, and these materials are also emerging as good catalysts for reactions such as NO reduction. This is an important field due to the increasing demands for environment-related high-temperature catalytic applications such as the cleansing of automobile exhaust gas.

The objective of this work was to synthesize \( Y₂Sn₇O₁₇ \) type pyrochlore compounds with A- and B-site substitution and also double substitution in the A site, by a hydrothermal method. These stannate pyrochlores produced were tested for NO reduction by CH₄, and selective removal of NO over Ba- and Ca-containing pyrochlores was also investigated.

2. Experimental procedure

2.1 Synthesis of pyrochlore oxide powders

The precursors for hydrothermal synthesis of \( Y₂Sn₇O₁₇ \) were prepared by coprecipitation from metal salt solutions. All chemicals used in this study were of reagent grade sup-
plied from Wako Pure Chemical Industries. Appropriate quantities of SnCl4·5H2O (Wako Pure Chemical Industries Ltd.), Ce(NO3)3·6H2O (Wako Pure Chemical Industries Ltd.), Cr(NO3)3·9H2O (Wako Pure Chemical Industries Ltd.), and Mn(NO3)2·6H2O (Wako Pure Chemical Industries Ltd.) were dissolved in deionized water. Amorphous coprecipitated gels were precipitated by addition of NH4OH at pH ~9 because the tin hydrous gel becomes soluble above pH 10. Then the solution was vigorously stirred for 24 h. The coprecipitated gels were then repeatedly washed and dispersed in deionized water before hydrothermal reaction.

To determine synthesis conditions for producing pure pyrochlore phase, the pH of the washed precursor suspension was adjusted to the pH ranging from 7 to 11 by NH4OH. The pH-adjusted feedstock was placed in a Teflon bottle with an inner volume of 25 cm³ held in a stainless-steel vessel followed by flushing with N2. After the vessel was sealed, hydrothermal reactions were performed at temperatures ranging from 110 to 190°C for 40 h using a 500-ml capacity autoclave with a magnetically driven stirrer (Model TPR-1, Taitsu Techno). After reaction, the resulting powders were repeatedly washed by centrifugation and decantation with deionized water to remove undesirables such as Cl⁻ and NO3⁻ following by drying in an oven for 24 h at 120°C.

2.2 Characterization

The crystalline phases were identified by X-ray diffractometry (XRD; Phillips APD 1700) using Cu Kα radiation at 40 kV and 40 mA with a monochromator over a 2θ range of 10–70° at a scan rate of 2°/min. The absorption state of NO was recorded as KBr pellets by Fourier transform infrared spectrometer (FT-IR; Shimadzu, Model 8200D). Morphology of the product particles was examined by scanning electron microscopy (SEM; JEOL JSM6330F) with an energy-dispersive X-ray (EDX) analyser (JEOL, JED-2001), while elemental distribution was investigated by selected-area EDX microanalyses with area sizes varying from 10 nm to 4 micrometers. EDX analysis confirms the presence of substituent elements. Particle size and surface area of the powders were also determined by a laser diffraction method (Nikkiso, Microtrac HRA 9320–X100/UPA 9340) and Brunauer–Emmett–Teller (B.E.T.) nitrogen adsorption technique (Coulter, Omnisorp 360), respectively. The powder density value was obtained using a Utracyprometer 1000 Version 2.12 at 110°C.

2.3 Evaluation of NO removal abilities

The catalytic tests were carried out in the steady-state flow mode. Sample powders of 200 mg were placed between quartz wool plugs in the reactor. The reactant gas mixture consisted of 0.1% NO and 0.2% CH₄ balanced by He at a space velocity (SV) of 20000 h⁻¹ was passed through the catalyst for NO reduction. For NO absorption/desorption experiments, a typical reactant blend of 800 ppm NO, 10% O₂, and He balance was passed through the catalyst while the reactor effluent gas was analyzed. The flow rate of each reactant gas was controlled by a mass flow controller (STEC Inc.). The flow of each gas was fixed and held constant with a 4-channel electronic mass-flow controller (UCAR Instruments, MFB–21–1). A temperature controller (Leeds & Northrup Instruments, Electromax V Plus) was used both for increasing the furnace temperature at linear heating rates (10 K/min) and for keeping the furnace at any selected value. For the catalytic reaction, the catalysts were pretreated in air at 800°C for 2 h. The total flow rate was 50 cm³·min⁻¹ over 0.2 g of catalyst (W/F = 0.24 g·s·cm⁻³). NO conversion to N₂ was evaluated using:

\[ \text{NO conversion to N}_2 \ (\%) = \left( \frac{[\text{N}_2]}{[\text{NO}]_{\text{in}}} \right) \times 100 \]

where [NO]in is the inlet NO concentration and [N₂] is the concentration of N₂ in the reactor effluent gas. Decomposition of the nitric oxide and total NO in the reactor effluent was detected using a chemiluminescence NO–NO₂ gas analyzer (Best Instruments, BCL–100 uH, BCU–100 uH). All other reactants were analyzed by on-line gas chromatography (Chrompack Micro–GC CP–2002). Blank experiments carried out by flowing the reactant streams over an empty reactor showed that no NO conversion occurred without catalyst.

3. Results and discussion

3.1 Synthesis of pyrochlore powders by hydrothermal method

Various synthesis processes of multicomponent powders with controlled morphology, size, and size distribution, against the different chemical reactivities between starting chemicals, have been reported. The reported processes, however, require complex steps and/or low concentrations of the starting chemicals. On the other hand, the hydrothermal process is known to be a method for the preparation of fine, high-purity, and homogeneous oxide powders. Crystalline powders form as a result of the interaction between the precursor and solution phases in hydrothermal synthesis. The pH of the solution mainly determines the chemical nature and its reaction of the solution species under a given thermodynamic condition. Therefore, the pH is a key variable in determining the phase composition of YₓSnₓOᵧ in the present study, similar to other hydrothermally derived powders such as PbTiO₃, PZT, BaTiO₃, TiO₂, and ZrO₂. Below the critical concentration for precipitation, the reaction product was amorphous with a minor phase of SnO₂. At pH 7, the reaction product was mainly amorphous with a minor phase of SnO₂. The amorphous gel started to crystallize into YₓSnₓCrₓOᵧ at pH 8. However, the crystallization process was sluggish, so that a mixture of poorly crystallized YₓSnₓOᵧ and the minor phases (SnO₂ and YCO₃OH) was detected. An increase in the pH facilitates crystallization of YₓSnₓOᵧ. The phase composition of the product obtained at pH 9 was identical to that obtained at pH 8, but crystallinity was higher. Crystalline YₓSnₓOᵧ with phase-pure pyrochlore structure was formed only when the pH of the hydrothermal reaction medium was above pH 10. At pH 11 or higher, highly crystalline YₓSnₓOᵧ was produced in less than 40 h.

To determine the lowest synthesis temperature, the precursors prepared at pH 10.3 were hydrothermally treated for 40 h at different temperatures ranging from 110 to 190°C. The reaction product at 110°C was amorphous, whereas crystalline YₓSnₓOᵧ was obtained at 160°C with a minor amount of SnO₂, as shown in Fig. 1. The impurity phase began to disappear above 160°C, and phase-pure pyrochlore YₓSnₓOᵧ was formed at 190°C. Recently, in our laboratory, well-defined LaₓSnₓOᵧ with a phase-pure pyrochlore structure has been synthesized by a hydrothermal process at temperatures as low as 200°C.

The X-ray diffraction patterns of the hydrothermally synthesized powders are shown in Fig. 2. X-ray powder measurements did not show the presence of any material other than the desired pyrochlore phases, except in the cases of YₓZrₓSnₓOᵧ, which had the YₓZrₓOᵧ phase with a small portion of cubic ZrO₂ and a trace amount of SnO₂ was detected for the YₓSnₓCeₓOᵧ compound.

The effect of the calcination temperature was investigated based on a phase analysis by X-ray diffraction, as shown in Figs. 3(A) and (B). It has been reported that the struc-
nature of Y2Sn2O7 remained consistently fully ordered over a temperature range of 25–1000°C.18) This phenomenon was also observed even after A- and B-site substitutions in this present study. However, Fig. 3(A) shows that as the calcination temperature increased, the diffraction lines grew and indicated the formation of crystalline SnO2 phase from 800°C, and were sharpened with increasing temperature only for the Ca-containing Ca0.8Sm1.2Sn1.8Ni0.2O7 compound. The crystallite size and the BET surface areas of synthesized powders are presented in Table 1.

SEM observation revealed that the synthesized particles have fairly spherical shapes with rough surfaces, as presented in Fig. 4. The sizes of the primary particulates were in the range of tens of nanometers. This indicates that the spherical shapes of powders are retained during hydrothermal treatment. In addition, the sources of A-site ions (barium or calcium) are incorporated and they are crystallized into the pyrochlore phases under hydrothermal conditions. Ba- and Ca-containing pyrochlore powders showed spherical shape, while all other powders have nearly spherical shape, as shown in Fig. 4. The particle size also has a relatively narrow distribution. Figure 5 shows transmission electron micrographs of the pyrochlore powders synthesized by hydrothermal treatment. The powders consisted of spherical secondary particles composed of small primary particulates.

3.2 NOx reduction activity of single- or double-substituted stannate pyrochlore powders

Figure 6 shows the temperature dependence of the NO reduction activity of stannate pyrochlores: (a) Y2Sn1.8Cr0.2O7, (b) Y1.8Sm0.2Sn1.8Cr0.2O7, (c) Y1.8Ce0.2Sn1.8Cr0.2O7, (d) Y1.8Eu0.2Sn1.8Cr0.2O7, (e) Y2Zr1.8Co0.2O7, (f) Ba0.8Y1.2Sn1.8Cr0.2O7, (g) Ba0.6Y1.2Sm0.2Sn1.8Cr0.2O7 and (h) Ca0.8Sm1.2Sn1.8Ni0.2O7. The activity appeared for all tested samples above 500°C and increased monotonically with increasing temperature in the presence of CH4. NO reduction activity was observed from a lower temperature region for Ce-doped Y1.8Ce0.2Sn1.8Cr0.2O7 catalyst. However, when only 2% O2 was present, the NO conversion rate decreased drastically to 3%–4% of that achieved with CH4. Teraoka et al.19) also observed excellent catalytic activity over tran-
The sorption–desorption characteristics of NO₂ were evaluated by heating the sample at a constant rate in the presence of a NO–O₂ mixture, as shown in Fig. 7. The broken line in the figure is the NO concentration in the feed gas, i.e., the concentration levels below and above this line indicate NO uptake and NO₂ desorption, respectively. The concentration of NO₂ was measured, using a NO₂ meter, as the sum of NO and NO₂ concentrations. The curves for both Ba₀.₆Y₁.₂Sm₀.₂Cr₀.₂O₇ and Ca₀.₈Sm₁.₂Sn₁.₈Ni₀.₂O₇ oxides initially showed complete removal of NO in the low-temperature region. Then, NO₂ desorption started at 250 and 400°C for Ba₀.₆Y₁.₂Sm₀.₂Cr₀.₂O₇ and Ca₀.₈Sm₁.₂Sn₁.₈Ni₀.₂O₇ oxides, respectively, and reached maxima at 310 and 460°C. The absorption behavior of Ba₀.₆Y₁.₂Sm₀.₂Sn₁.₈Cr₀.₂O₇ was basically the same as that of Ba₀.₆Y₁.₂Sm₁.₈Cr₀.₂O₇, except for a difference in the overall amount of absorption. At elevated temperatures, the desorption curve approached the initial concentration level as absorption/desorption proceeded. In the presence of gaseous O₂, absorption of NO by this reaction was enhanced. The enhancement of NO removal by O₂ strongly suggests that the absorption proceeds via oxidation of NO₂. The NO removal is, therefore, attributed to catalytic oxidation and subsequent absorption of NO, where nitrate-related compounds are probably formed in the oxides.

The reversibility of the absorption and desorption of the Ba₀.₆Y₁.₂Sm₀.₂Sn₁.₈Cr₀.₂O₇ oxide was tested by repeating the absorption of NO at 200°C and desorption at 450°C in He. The phenomenon of absorption/desorption is perfectly reproducible and can be repeated many times without deactivation. Although the absorption capacity of the first absorption experiment after a heat treatment at 475°C was the highest, it then decreased and was almost constant from the 2nd cycle, indicating that absorption and thermal desorption was almost reversible. The amount of absorption at the fifth absorption step decreased to approximately 85% of that at the first step. This decrease may have resulted from a decrease in the surface area, or grain growth of tin oxide and substituted transition metal oxides.

As mentioned above, the high absorption rate and capacity are generally attained using more basic components. The alkaline earth is effective in this respect. However, the use of the bulk alkaline or rare earth compounds implies deactivation due to the formation of stable carbonate in the presence of CO₂. In this respect, reversibility of Ba₀.₆Y₁.₂Sn₁.₈Cr₀.₂O₇ catalyst in CO₂-containing atmosphere is an attractive advantage. It was also observed that the activity of Ba₀.₆Y₁.₂Sm₀.₂Sn₁.₈Cr₀.₂O₇ for NO absorption was not decreased despite a CO₂ content of 5%, and this activity remained constant even when the time of exposure to the lean-burn mixture was longer than 4 h. This proves that if barium is incorporated into a well-defined crystallographic structure, it is protected against deactivation by carbonation. Moreover, it has been reported that if barium has a strong bond with aluminum or tin, it will be protected against carbonation.

An FT–IR spectrum of the Ba₀.₆Y₁.₂Sm₀.₂Sn₁.₈Cr₀.₂O₇ sample was recorded before and after exposure to NO in O₂ by the KBr method. The spectrum after NO sorption clearly indicated the appearance of the absorption band at around 1385 cm⁻¹ (Fig. 8). The sharp band is attributed to the nitrate ion, NO₃⁻, on the solid. Therefore, the removal of NO by this system proceeds by oxidation of NO to NO₃⁻ ions on the solid surface. The IR band for the Ba₀.₆Y₁.₂Sm₀.₂Sn₁.₈Cr₀.₂O₇ oxide before the absorption treatment after heating at 475°C exhibited a small band at 1385 cm⁻¹. This band is assigned to the v₁ stretching band of the NO₃⁻ ion which ex-
hibits the strongest peak in most nitrates, whereas other bending bands in the low-wave-number region could not be clearly observed due to the overlap with the band of the oxide. Residual nitrate ions seem to be present even after heat treatment at 475°C. The intensity of this band increased after the absorption of NO for 10 h.

The effect of the contact time (W/F) was also investigated, where W is the weight of the Ba$_{0.6}$Y$_{1.2}$Sm$_{0.2}$Sn$_{1.8}$Cr$_{0.2}$O$_7$ oxide and F is the total flow rate. NO removal was almost constant for contact times of 1.0, 0.5, and 0.24 g·s·cm$^{-3}$ at the start of absorption, whereas it decreased sharply in the case of W/F=0.12 g·s·cm$^{-3}$. Since a high flow rate led to a rapid saturation of absorption, the total absorption capacity was unchanged with W/F. The contact time and NO concentration did not affect the overall absorption capacity under the present experimental conditions, and the initial NO removal was high in every case. Therefore, the absorption was regarded as being very rapid. Such rapid absorption is favorable for practical applications of the NO-removal system.

4. Conclusions

The preparation of uniform A- and B-site-substituted yttrium tin oxide with a phase-pure pyrochlore structure at temperatures as low as 200°C has been demonstrated. For the formation of pyrochlore, the pH of the initial hydrothermal reaction medium must be above 10. The methodology presented in this work provides a simple method for preparing spherical pyrochlore oxide powder with a high surface area. Pyrochlore compounds have been developed as potential catalysts for NO traps and have revealed interesting properties because their trapping capacity is high and the temperature of both absorption and desorption are in a

Fig. 4. Typical SEM micrograph of (A) Ca$_{0.8}$Sm$_{1.2}$Sn$_{1.8}$Ni$_{0.2}$O$_7$, (B) Ba$_{0.6}$Y$_{1.2}$Sm$_{0.2}$Sn$_{1.8}$Cr$_{0.2}$O$_7$ (high magnification), (C) Ba$_{0.6}$Y$_{1.2}$Sm$_{0.2}$Sn$_{1.8}$Cr$_{0.2}$O$_7$ (low magnification) and (D) Y$_2$Sn$_{1.8}$Cr$_{0.2}$O$_7$ pyrochlore powders.

Fig. 5. TEM micrographs for the synthesized (A) Ba$_{0.6}$Y$_{1.2}$Sm$_{0.2}$Sn$_{1.8}$Cr$_{0.2}$O$_7$ (high magnification) and (B) Ba$_{0.6}$Y$_{1.2}$Sm$_{0.2}$Sn$_{1.8}$Cr$_{0.2}$O$_7$ (low magnification) at 190°C, pH 10.3 under hydrothermal conditions.
Hydrothermal Synthesis of New Compounds with the Pyrochlore Structure and Its Application to Nitric Oxide Abatement

Fig. 6. NO conversion as a function of temperature over several pyrochlore oxide catalysts. The reaction was run at a space velocity of 20000 h\(^{-1}\) and flow rate of 50 cm\(^3\) min\(^{-1}\) with 1000 ppm NO, 2000 ppm CH\(_4\), He balance.

Fig. 7. Absorption-desorption curves of NO by (●) Ca\(_{0.8}\)Sm\(_{1.2}\)Sn\(_{1.8}\)Ni\(_{0.2}\)O\(_7\) and (□) Ba\(_{0.6}\)Y\(_{1.2}\)Sn\(_{1.8}\)Cr\(_{0.2}\)O\(_7\) pyrochlore oxide during programmed heating. The reaction was run at a space velocity of 20000 h\(^{-1}\) and flow rate of 50 cm\(^3\) min\(^{-1}\) with 800 ppm NO, and 10% O\(_2\), He balance, heating rate=5°C min\(^{-1}\), (---) initial concentration of NO.

Fig. 8. FT-IR spectra of Ba\(_{0.6}\)Y\(_{1.2}\)Sm\(_{1.2}\)Sn\(_{1.8}\)Cr\(_{0.2}\)O\(_7\) oxide (a) after heating in air at 475°C and (b) after absorption of NO at 200°C.

range relevant for industrial applications.

Acknowledgments This work has been supported by METI, Japan, as part of the Synergy Ceramics Project. The work is also partly supported by NEDO. The authors are members of the Joint Research Consortium of Synergy Ceramics.

References