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

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パイロクロア構造を有する新化合物の水熱合成及びその NO_x 浄化特性

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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) Y₂Sn_{1.8}Cr_{0.2}O₇, (b) Y_{1.8}Sm_{0.2}Sn_{1.8}Cr_{0.2}O₇, (c) Y_{1.8}Ce_{0.2}Sn_{1.8}Cr_{0.2}O₇, (d) Y_{1.8}Eu_{0.2}Sn_{1.8}Cr_{0.2}O₇, (e) Y₂Zr_{1.8}Co_{0.2}O₇, (f) Ba_{0.8}Y_{1.2}Sn_{1.8}Cr_{0.2}O₇, (g) Ba_{0.6}Y_{1.2}Sm_{0.2}Sn_{1.8}Cr_{0.2}O₇ and (h) Ca_{0.8}Sm_{1.2}Sn_{1.8}Ni_{0.2}O₇. 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 NO_x 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.

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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.¹⁾ 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, Pb, 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.²⁾ 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 stream³⁾ or by a two-stage operation whereby NO_x is trapped on a selective sorbent, and then reduced by a short fuel excursion.⁴⁾ The key point in the latter strategy is the efficiency of NO_x absorption materials; they should adsorb (or absorb) a large quantity of NO_x in a high space velocity gas stream containing both CO₂ and H₂O in the temperature range of 25–350°C. Belyaev et al.⁵⁾ 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.⁶⁾ reported that if barium is incorporated in a well-defined structure presenting nanocrystallinity, NO_x 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.⁷⁾ If this perovskite is doped with potassium (La_{0.8}K_{0.2})MnO₃, molecular and dissociative adsorption of NO is observed.⁸⁾ Alternatively, if barium is incorporated as the cation at the A-site in the pyrochlore (A₂B₂O₇), 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.⁹⁾ Moreover, due to the basic nature of yttrium oxide, it has more recently been found to be an effective catalyst for methane dimerization¹⁰⁾ and the selective catalytic reduction of nitrogen oxide.¹¹⁾ 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.¹²⁾ 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 Y₂Sn₂O₇-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 Y₂Sn₂O₇ 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 $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ (Wako Pure Chemical Industries Ltd.), $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Wako Pure Chemical Industries Ltd.), $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Wako Pure Chemical Industries Ltd.), and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Wako Pure Chemical Industries Ltd.) were dissolved in deionized water. Amorphous complex gels were precipitated by addition of NH_4OH 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 redispersed 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 NH_4OH . The pH-adjusted feedstock was placed in a Teflon bottle with an inner volume of 25 cm^3 held in a stainless-steel vessel followed by flushing with N_2 . 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, Taiatsu Techno). After reaction, the resulting powders were repeatedly washed by centrifugation and decantation with deionized water to remove undesirable anions such as Cl^- and NO_3^- followed 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 $\text{Cu K}\alpha$ radiation at 40 kV and 40 mA with a monochromator over a 2θ range of $10\text{--}70^\circ$ at a scan rate of $2^\circ/\text{min}$. The absorption state of NO_x 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 substitute 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 Ultrapycnometer 1000 Version 2.12.

2.3 Evaluation of NO_x 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% CH_4 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% O_2 + He balance was passed through the catalyst while the temperature was linearly increased or decreased in the temperature range of $100\text{--}650^\circ\text{C}$ with 1 h isothermal steps at any selected temperature during which the effluent gas was analysed. 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 it constant at any selected value. Before the catalytic reaction, the catalysts were pretreated in air at 800°C for 2 h. The total flow rate was $50\text{ cm}^3 \cdot \text{min}^{-1}$ over 0.2 g of catalyst ($W/F = 0.24\text{ g} \cdot \text{s} \cdot \text{cm}^{-3}$). NO conversion to N_2 was

evaluated using:

$$\text{NO conversion to } \text{N}_2 (\%) = \{2[\text{N}_2]/[\text{NO}]^{\text{in}}\} \times 100,$$

where $[\text{NO}]^{\text{in}}$ is the inlet NO concentration and $[\text{N}_2]$ is the concentration of N_2 in the reactor effluent gas. Decomposition of the nitric oxide and total NO_x in the reactor effluent was detected using a chemiluminescent $\text{NO}\text{--}\text{NO}_x$ 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_x 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.^{(13),(14)} The reported processes, however, require complex steps and/or low concentrations of the starting chemicals.⁽¹⁵⁾ On the other hand, the hydrothermal process is known to be a method for the preparation of fine, high-purity, and homogeneous oxide powders.⁽¹⁾ 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 $\text{Y}_2\text{Sn}_2\text{O}_7$ in the present study, similar to other hydrothermally derived powders such as PbTiO_3 , PZT , BaTiO_3 , TiO_2 , and ZrO_2 .⁽¹⁶⁾ Below the critical concentration for precipitation, the reaction product was amorphous with a minor phase of SnO_2 . At pH 7, the reaction product was again mainly amorphous with a minor phase of SnO_2 . The amorphous gel started to crystallize into $\text{Y}_2\text{Sn}_{1.8}\text{Cr}_{0.2}\text{O}_7$ at pH 8. However, the crystallization process was sluggish, so that a mixture of poorly crystallized $\text{Y}_2\text{Sn}_2\text{O}_7$ and the minor phases (SnO_2 and YCO_3OH) was detected. An increase in the pH facilitates crystallization of $\text{Y}_2\text{Sn}_2\text{O}_7$. The phase composition of the product obtained at pH 9 was identical to that obtained at pH 8, but crystallinity was higher. Crystalline $\text{Y}_2\text{Sn}_2\text{O}_7$ 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 $\text{Y}_2\text{Sn}_2\text{O}_7$ 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 $\text{Y}_2\text{Sn}_2\text{O}_7$ was obtained at 160°C with a minor amount of SnO_2 , as shown in Fig. 1. The impurity phase began to disappear above 160°C , and phase-pure pyrochlore $\text{Y}_2\text{Sn}_2\text{O}_7$ was formed at 190°C . Recently, in our laboratory, well-defined $\text{La}_2\text{Sn}_2\text{O}_7$ with a phase-pure pyrochlore structure has been synthesized by a hydrothermal process at temperatures as low as 200°C .⁽¹⁷⁾

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 $\text{Y}_2\text{Zr}_{1.8}\text{Co}_{0.2}\text{O}_7$, which had the YZrO_3 phase with a small portions of cubic ZrO_2 and a trace amount of SnO_2 was detected for the $\text{Y}_{1.8}\text{Eu}_{0.2}\text{Sn}_{1.8}\text{Cr}_{0.2}\text{O}_7$ 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-

Fig. 1. XRD patterns of the product prepared as a function of synthesis temperature in solution with pH 10.30 reacted for 40 h.

Fig. 2. X-ray diffraction pattern of several hydrothermally derived pyrochlore oxide powders with A- and B-site substitutions.

ture of $Y_2Sn_2O_7$ 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 SnO_2 phase from 800°C, and were sharpened with increasing temperature

Fig. 3. X-ray diffraction pattern of (A) $Ca_{0.8}Sm_{1.2}Sn_{1.8}Ni_{0.2}O_7$ and (B) $Y_{1.8}Sm_{0.2}Sn_{1.8}Cr_{0.2}O_7$ pyrochlore showing phase stability behavior as a function of temperature.

only for the Ca-containing $Ca_{0.8}Sm_{1.2}Sn_{1.8}Ni_{0.2}O_7$ 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 NO_x 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) $Y_2Sn_{1.8}Cr_{0.2}O_7$, (b) $Y_{1.8}Sm_{0.2}Sn_{1.8}Cr_{0.2}O_7$, (c) $Y_{1.8}Ce_{0.2}Sn_{1.8}Cr_{0.2}O_7$, (d) $Y_{1.8}Eu_{0.2}Sn_{1.8}Cr_{0.2}O_7$, (e) $Y_2Zr_{1.8}Co_{0.2}O_7$, (f) $Ba_{0.8}Y_{1.2}Sn_{1.8}Cr_{0.2}O_7$, (g) $Ba_{0.6}Y_{1.2}Sm_{0.2}Sn_{1.8}Cr_{0.2}O_7$ and (h) $Ca_{0.8}Sm_{1.2}Sn_{1.8}Ni_{0.2}O_7$. The activity appeared for all tested samples above 500°C and increased monotonically with increasing temperature in the presence of CH_4 . NO reduction activity was observed from a lower temperature region for Ce-doped $Y_{1.8}Ce_{0.2}Sn_{1.8}Cr_{0.2}O_7$ catalyst. However, when only 2% O_2 was present, the NO conversion rate decreased drastically to 3%–4% of that achieved with CH_4 . Teraoka et al.¹⁹⁾ also observed excellent catalytic activity over tran-

Table 1. Particle Characteristics of a Number of Hydrothermally Derived Oxide Pyrochlore Stannates of the Type $Y_2Sn_2O_7$ with A- and B-Site Substitutions

Reaction Conditions		
Concentration	0.1M	
Stirring Speed	500 rpm	
Reaction Time	40 h	
Temperature	190°C at pH 10.30	
	Particle Size (μm) $d_{50\%}$	Surface Area (m^2/g)
=====		
$Y_2Sn_{1.8}Cr_{0.2}O_7$ 800°C	1.1041	35.18
$Y_{1.8}Sm_{0.2}Sn_{1.8}Cr_{0.2}O_7$ 800°C	1.0111	40.12
$Y_{1.8}Ce_{0.2}Sn_{1.8}Cr_{0.2}O_7$ 800°C	1.2255	43.28
$Y_{1.8}Eu_{0.2}Sn_{1.8}Cr_{0.2}O_7$ 800°C	1.3451	34.18
$Y_2Zr_{1.8}Co_{0.2}O_7$ 800°C	2.1345	26.36
$Ba_{0.6}Y_{1.2}Sm_{0.2}Sn_{1.8}Cr_{0.2}O_7$ 475°C / 4 h	1.1456	61.59
800°C / 1 h	2.1450	22.44
$Ba_{0.8}Y_{1.2}Sn_{1.8}Cr_{0.2}O_7$ 475°C / 4 h	1.3456	58.59
800°C / 1 h	2.3441	23.94
$Ca_{0.8}Sm_{1.2}Sn_{1.8}Ni_{0.2}O_7$ 475°C / 4 h	1.5456	42.87
800°C / 1 h	2.38441	17.94

sition-metal-substituted $La_2Sn_2O_7$ pyrochlore under non-oxidizing atmosphere.

NO reduction by CH_4 is considered to be a key reaction for NO_x removal from automotive exhaust. A number of authors have examined the mechanism of this reaction and different reaction pathways have been suggested. However, methane can react not only with nitric oxide but also with O_2 via combustion as follows:

and

Besides the nitric oxide reduction reactions (Eqs. 1 and 2), CH_4 also reacts with oxygen (Eq. 3). Since NO reduction was carried out in the absence of oxygen, Eq. 1 prevails in this study.

A promotional effect of CH_4 on NO conversion to N_2 might be expected since CH_4 can facilitate the removal of surface oxygen via the reduction of nitrogen oxide species. Indeed, CO_2 was observed instead of O_2 in the presence of CH_4 , indicating an interaction between CH_4 and surface oxygen.

3.3 Sorption/desorption of NO during heating

Recently, it has been reported that if barium is incorporat-

ed in a well-defined structure presenting nanocrystallinity, NO_x storage is possible with high absorption/desorption capacities.^{6),20),21)} The sorption-desorption characteristics of NO_x were evaluated by heating the sample at a constant rate in the presence of a $NO-O_2$ 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 NO_x desorption, respectively. The concentration of NO_x was measured, using a NO_x meter, as the sum of NO and NO_2 concentrations. The curves for both $Ba_{0.6}Y_{1.2}Sm_{0.2}Sn_{1.8}Cr_{0.2}O_7$ and $Ca_{0.8}Sm_{1.2}Sn_{1.8}Ni_{0.2}O_7$ oxides initially showed complete removal of NO in the low-temperature region. Then, NO_x desorption started at 250 and 400°C for $Ba_{0.6}Y_{1.2}Sm_{0.2}Sn_{1.8}Cr_{0.2}O_7$ and $Ca_{0.8}Sm_{1.2}Sn_{1.8}Ni_{0.2}O_7$ oxides, respectively, and reached maxima at 310 and 460°C. The absorption behavior of $Ba_{0.6}Y_{1.2}Sm_{0.2}Sn_{1.8}Cr_{0.2}O_7$ was basically the same as that of $Ba_{0.8}Y_{1.2}Sn_{1.8}Cr_{0.2}O_7$, 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 O_2 , absorption of NO by this reaction was enhanced. The enhancement of NO removal by O_2 strongly suggests that the absorption proceeds via oxidation of NO. 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 $Ba_{0.6}Y_{1.2}Sm_{0.2}Sn_{1.8}Cr_{0.2}O_7$ 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 degradation due to the formation of stable carbonate in the presence of CO_2 .²²⁾ In this respect, reversibility of $Ba_{0.6}Y_{1.2}Sm_{0.2}Sn_{1.8}Cr_{0.2}O_7$ catalyst in CO_2 -containing atmosphere is an attractive advantage. It was also observed that the activity of $Ba_{0.6}Y_{1.2}Sm_{0.2}Sn_{1.8}Cr_{0.2}O_7$ for NO absorption was not decreased despite a CO_2 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 aluminium or tin, it will be protected against carbonation.²²⁾

An FT-IR spectrum of the $Ba_{0.6}Y_{1.2}Sm_{0.2}Sn_{1.8}Cr_{0.2}O_7$ sample was recorded before and after exposure to NO in O_2 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, NO_3^- , on the solid. Therefore, the removal of NO by this system proceeds by oxidation of NO to NO_3^- ions on the solid surface. The IR band for the $Ba_{0.6}Y_{1.2}Sm_{0.2}Sn_{1.8}Cr_{0.2}O_7$ oxide before the absorption treatment after heating at 475°C exhibited a small band at 1385 cm^{-1} . This band is assigned to the ν_3 stretching band of the NO_3^- ion which ex-

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

Fig. 5. TEM micrographs for the synthesized (A) $\text{Ba}_{0.6}\text{Y}_{1.2}\text{Sm}_{0.2}\text{Sn}_{1.8}\text{Cr}_{0.2}\text{O}_7$ (high magnification) and (B) $\text{Ba}_{0.6}\text{Y}_{1.2}\text{Sm}_{0.2}\text{Sn}_{1.8}\text{Cr}_{0.2}\text{O}_7$ (low magnification) at 190°C , pH 10.3 under hydrothermal conditions.

hibits the strongest peak in most nitrates,²³⁾ 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 $\text{Ba}_{0.6}\text{Y}_{1.2}\text{Sm}_{0.2}\text{Sn}_{1.8}\text{Cr}_{0.2}\text{O}_7$ oxide and F is the total flow rate. NO removal was almost constant for contact times of 1.0, 0.5, and $0.24\text{ g}\cdot\text{s}\cdot\text{cm}^{-3}$ at the start of absorption, whereas it decreased sharply in the case of $W/F = 0.12\text{ g}\cdot\text{s}\cdot\text{cm}^{-3}$. 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_x traps and have revealed interesting properties because their trapping capacity is high and the temperature of both absorption and desorption are in a

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 cm³ min⁻¹ with 1000 ppm NO, 2000 ppm CH₄, He balance.

Fig. 8. FT-IR spectra of Ba_{0.6}Y_{1.2}Sm_{0.2}Sn_{1.8}Cr_{0.2}O₇ oxide (a) after heating in air at 475°C and (b) after absorption of NO at 200°C.

Fig. 7. Absorption-desorption curves of NO_x by (●) Ca_{0.8}Sm_{1.2}Sn_{1.8}Ni_{0.2}O₇ and (▽) Ba_{0.6}Y_{1.2}Sm_{0.2}Sn_{1.8}Cr_{0.2}O₇ pyrochlore oxide during programmed heating. The reaction was run at a space velocity of 20000 h⁻¹ and flow rate of 50 cm³ min⁻¹ with 800 ppm NO, and 10% O₂, He balance, heating rate = 5°C min⁻¹, (---) initial concentration of NO.

range relevant for industrial applications.

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