Studies on catalytic and structural properties of BaRuO3 type perovskite material for diesel soot oxidation

Pradeep Doggali, Fabien Grasset, Olivier Cador, S. Rayalu, Yasutake Teraoka, Nitin Labhsetwar

To cite this version:
Pradeep Doggali, Fabien Grasset, Olivier Cador, S. Rayalu, Yasutake Teraoka, et al.. Studies on catalytic and structural properties of BaRuO3 type perovskite material for diesel soot oxidation. Journal of Environmental Chemical Engineering, 2014, 2, pp.340-343. <10.1016/j.jece.2014.01.002>. <hal-00974714>

HAL Id: hal-00974714
https://hal.archives-ouvertes.fr/hal-00974714
Submitted on 2 Jun 2014

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Studies on catalytic and structural properties of BaRuO$_3$ type perovskite material for diesel soot oxidation

Pradeep Doggali, F. Grasset$^a$, O. Cador$^a$, S. Rayalu, Y. Teraoka$^b$ and Nitin Labhsetwar$^*$

CSIR- National Environmental Engineering Research Institute,
(CSIR-NEERI), Nehru Marg, Nagpur, 440020 India

$^a$UMR Science Chimiques de Rennes UR1-CNRS 6226, Université de Rennes 1, Campus de Beaulieu, CS74205, F-35042 Rennes Cedex (France)

$^b$Department of Energy and Material Sciences, Faculty of Engineering Sciences, Kyushu University, Kasuga, Fukuoka 816-8580, Japan

* Author for correspondence: E-mail: nk_labhsetwar@neeri.res.in
Tel: 0091-712-2249885-90; Fax: 0091-712-2249900

Postal address:
Dr. Nitin Labhsetwar,
Senior Principal Scientist,
CSIR-National Environmental Engineering Research Institute (CSIR-NEERI)
Nehru Marg, NAGPUR-440020, India
Abstract

BaRuO$_3$ based perovskite type catalytic material was synthesized by co-precipitation method and its catalytic activity has been tested for diesel soot oxidation. This material shows high catalytic activity for carbon/soot oxidation reaction with lowering of carbon oxidation temperature by $>190$ °C. The catalytic activity could be due to dissociative adsorption of oxygen on BaRuO$_3$ surface. It is postulated by structural investigations that 120 planes of BaRuO$_3$ can have abundant Ru atoms which, can facilitate the oxygen dissociation. The additional advantage of using Ru in BaRuO$_3$ is the thermal stability of Ru in oxide matrix as well as basicity offered by Ba. These synergetic effects can also be responsible for the high soot/carbon oxidation activity of this perovskite type material, which can be a potential candidate for control of soot emissions from combustion processes and vehicle exhaust.

**Key words**: BaRuO$_3$, perovskite, diesel soot oxidation, vehicular exhaust emission control.
1. Introduction

Particulate matter (PM) emissions from diesel engines are harmful due to both their chemical composition and particle size [1, 2]. The diesel particulate filter (DPF) has so far been the most potential technological option for the effective control of diesel PM emissions, however, its regeneration possibly at the exhaust temperature appears to be the only but difficult limitation. Although, NOx based catalyst assisted passive regenerative type DPFs have been developed, soot oxidation by oxygen/air remains focus of intense research to avoid the NOx dependency for regeneration. Considerable success has been achieved in development of new catalytic materials and the possible mechanisms for the direct soot oxidation by oxygen [3, 4]. As diesel exhaust temperature is substantially lower than the soot oxidation light-off temperature, development of active catalytic materials is still a challenging issue and demand for the investigations on new catalytic materials. Ruthenium in its metallic, coordinated and oxide forms is a good catalytic material for several reactions of commercial and environmental importance [5, 6]. It is an excellent oxidation catalyst [7]. Nevertheless, its catalytic applications for high temperature oxidation reactions and automobile exhaust treatment could not find much practical success mainly due to its relatively inferior thermal stability. Ruthenium dioxide (RuO$_2$) has a tendency to get oxidized in to higher oxides, which are of volatile nature at temperature beyond 800$^\circ$C [8]. This has often been a limitation for its high temperature applications, including catalytic applications. Also, there are very limited tailoring possibilities with RuO$_2$ to alter its catalytic properties for specific reactions. Ruthenium can be stabilized in ABO$_3$ type perovskite material structure, which offers good thermal stability as well as catalytic material properties due to its structural and chemical specifications [9].
With more reliable findings on effective dissociative adsorption of oxygen on Ru surface, the interest in catalytic properties of Ru based materials has been rejuvenated for academic as well as practical reasons [10]. BaRuO$_3$, one of the relatively simple and stable Ru based oxides, crystallizes in hexagonal perovskite material structure consisting of face sharing octahedra [11]. The hexagonal BaRuO$_3$ provides an example of the complex oxide based on closed packed stacking of BaO layers of perovskite type material structure. The physical properties of BaRuO$_3$ compound are mainly due to unfilled 4 d level of Ru ions, however, the ionic radii of Ba cation also play a significant role [11]. Presence of ruthenium in 4+ stable oxidation state and possible influence of Ba on the catalytic active Ru makes this compound a potential material for catalytic studies. The properties of ruthenium based perovskite type materials for their catalytic applications have been seldom investigated, although theoretically they can be potential catalytic materials for various reactions including oxidation reactions. We have been successful in development of new and improved methods for the synthesis of lanthanum based perovskite type ruthenate materials, which show high thermal stability and catalytic properties [9, 12-14]. As ruthenium is relatively much cheaper (about 18 times than Pt, 10 times than Pd and 12 times to that of Rh) metal than other Platinum Group Metals (PGM), its use in autho-exhaust emission control can be justified.

In this work, we report the catalytic properties of BaRuO$_3$ type perovskite material with high catalytic activity for carbon/soot oxidation reaction, probably for the first time. It was possible to understand certain structure-property relations through the structural models as well as the chemical composition of this material. The activity and stability results of BaRuO$_3$ can help rejuvenating ruthenium based perovskites for important applications in environmental catalysis.

2. Experimental

2.1. Synthesis of BaRuO$_3$
Co-precipitation has been widely used for the synthesis of a large number of perovskites. In the present method, Ba$^{2+}$ and Ru$^{3+}$ precursors were dissolved in deionized water and subsequently mixed together. The mixed metal ion solution was slowly added with constant stirring, to aqueous mixed alkali solution. A mixed alkali solution was prepared by mixing 500 ml each of 1M aqueous ammonium carbonate solution and 500 ml of 1 N aqueous ammonia solution. The precipitate thus obtained was allowed to settle for 5 h followed by filtration and washings with de-ionized water and oven drying at 70 °C. The resultant mass was heated at 500 °C for 5 h followed by grinding and further heating at 800 °C for 6 h.

2.2. Characterization

XRD patterns were recorded on a Rigaku Rint-220HF diffractometer, operated at 40 kV and 50 mA with a monochromator and using Cu Kα radiations ($\lambda =0.15418$ nm). Indexing of XRD peaks was done, by using JCPDS database for the respective phases. Surface area was measured by nitrogen adsorption method using automatic gas adsorption apparatus BELSORP 28SA (produced by Nippon Bell Co.) and data were evaluated by BET method. The samples were pre-treated at 300 °C before the nitrogen adsorption experiments. Thermal stability experiments were performed by heating the material at 900 °C, under air atmospheres and also performed using TGA technique (Rigaku-TAS-200 apparatus) in the same temperature range, mainly to study the possibility of thermal loss by the formation of volatile ruthenium oxides.

2.3. Catalytic Evaluations

The synthesized BaRuO$_3$ was evaluated for its carbon/soot oxidation activity following a batch type temperature programmed reaction procedure using activated carbon. 100 mg of carbon-catalyst (ca. 5wt%) mixture was homogenized in an agate lines mortar pestle, pelletized (tight contact condition) and sieved to 20-100 mesh. The pellets were placed in a fixed bed flow reactor
with a programmable heater controller. A gas mixture containing 15% oxygen was flown with the increasing temperature with a predetermined heating cycle. Gas analysis was carried out using an auto-sampling PC controlled, MTI-P-200, Shimadzu GC system with molecular sieve and Porapak-Q and molecular sieve columns. The activation energy has been estimated by using Ozawa method by proper interpretation of TGA data. The thermo gravimetric analysis experiments were performed under loose contact condition wherein the mixture of soot and catalysts were heated from 35 to 800°C at different heating rates, in air atmosphere. According to the Ozawa Method, the following relationship links the values of the heating rate \( \ln(\phi) \) with the corresponding values of temperature \( T_\alpha \) at which a fixed fraction of carbon is burned during each run;

\[
\ln(\phi) = 1.052(E/R)(1/T_\alpha) + A
\]

Where, \( A \) is a constant, \( E \) is activation energy (kJ mole\(^{-1}\)) and \( R \) is ideal gas constant (8.314 J/mole/K) [15, 16]. In this case, TGA experiments were performed using the loose contact method by shaking the mixture of catalyst and carbon (90:10) in a glass bottle for five minutes. This method is often used as a loose contact method for catalytic soot oxidation experiments.

3. Results and discussion

The synthesized BaRuO\(_3\) has three crystallographic forms representative of the "hexagonal perovskite". These different forms depending of the pressure parameters, are known as the 9R, 4H and 6H layers. At ambient pressure, BaRuO\(_3\) has been found to adopt the 9-layers repeat sequence (chh)\(_3\). 9R-BaRuO\(_3\) crystallizes in the Rhombohedral space group R-3m (unit cell \( a = 5.75 \) A and \( c=21.60 \) A). The structure consists of trimers of face sharing octahedra, which are joined via terminal corners to constitute a three-dimensional network [11]. The XRD analysis (Fig. 1) confirms the formation of single phase, crystalline BaRuO\(_3\) and infers that BaRuO\(_3\) can be easily synthesized by co-precipitation method with good purity and crystallinity. The BET-surface area
result of synthesized BaRuO$_3$ is observed to be 5 m$^2$/g, which is in the expected range, considering the high synthesis temperature used, leading to sintering of material. The barium and ruthenium contents of the catalyst were determined using ICP-OES technique (Perkin–Elmer, Model Optima 4100DV). Blank experiments were performed throughout the studies and majority of the experiments were repeated thrice and it was observed that the experimental error was within ±2%. The samples were dissolved in acid before the analysis. The BaRuO$_3$ sample was then studied for its thermal stability as RuO$_2$ suffers thermal loss due to the formation of volatile oxides. The post-heated material shows practically no change in the XRD pattern, thereby confirming the unchanged structure and crystallinity of the material, while practically no weight loss was observed during heating the materials on a TGA machine. It can therefore be inferred that Ru can be thermally stabilized as BaRuO$_3$ in perovskite structure, under the oxidative atmosphere.

3.1. Catalytic activity

Diesel particulate (soot) consists of carbon core associated with hydrocarbons including polyaromatic hydrocarbons (PAH) and nitro-PAH, sulfates, water, trace amounts of other metals [17]. The non-catalytic combustion temperature of soot generally exceeds 550 °C, however, this depends on various factors. Therefore, model soot/carbons are generally used for laboratory studies, which offer much better reproducibility than the natural soot. The model soot/carbons used in this study are activated carbon (for fixed bed evaluations) with following physicochemical properties: fraction of adsorbed hydrocarbons (5.2%), ash (<0.14%), C (94.2%), H (0.4%), N (0.3%), S (0.5%) and carbon black (Degussa S.A. Printex) for TGA based evaluations.

The carbon oxidation activity results for bare activated carbon using temperature programmed oxidation (TPO) are presented in Fig. 2a. These results suggest that the T$_i$
(Temperature at which carbon oxidation initiated) of the non catalyzed oxidation of carbon starts above 400 °C and effective soot oxidation was observed only after 540°C with $T_I$ (Temperature at which carbon oxidation completed) at 650 °C. TPO results for BaRuO$_3$ assisted activated carbon oxidation (Fig. 2b) suggest that the carbon oxidation with BaRuO$_3$ catalyst shows two peaks in the temperature range of 200–480 °C. This initial oxidation (first peak) can be attributed to the catalytic oxidation of soluble organic fraction (SOF) component, which is an exothermic reaction. The exothermic heat generated during oxidation of SOF fraction also leads to carbon oxidation, especially the carbon part in close contact with catalyst particles. Therefore, the first peak could be correlated to combined effect of SOF oxidation as well as carbon oxidation promoted by exothermic heat of SOF oxidation and that in closer contact with catalyst particles.

The second peak appeared at 300 °C could be due to the release of CO$_2$ as a result of carbon oxidation without substantial SOF content and with relatively weaker contacts. The $T_I$ and $T_f$ of catalyst assisted soot oxidation were observed to be around 200 °C and 435 °C, respectively. These results show decrease in $T_I$ value by about 200 °C and $T_f$ by 215 °C with catalyst assisted carbon oxidation as compared to non-catalyzed activated carbon oxidation. Such results confirm high catalytic activity of BaRuO$_3$ in absence of NO$_x$. Soot oxidation is usually facilitated by presence of NO$_2$ at low temperatures following the formation of NO oxidation to NO$_2$. The observed lowering of carbon oxidation temperature in absence of NO$_2$ is therefore quite significant [18-23], and thus the present BaRuO$_3$ catalyst shows excellent catalytic activity considering it’s very low surface area. This observation also support that the micro surface area is not very important in case of oxygen based soot/carbon oxidation considering the fact that both catalyst and a reactant are in solid state. There was practically no CO generation, which is sometimes present as a product of incomplete combustion. The XRD analysis of post-heated
sample at 900 °C does not show any change as compared to that of original material. This confirms the high thermal stability of BaRuO₃, otherwise RuO₂ and Ru metal are well known to show thermal loss at such high temperatures in oxidative atmosphere. Such batch experiments using the air or simulated exhaust flow offer relatively more realistic conditions of catalyst use for DPF (Diesel particulate filter) regeneration as compared to thermo gravimetric analysis (TGA) based evaluations. The activation energy for catalyzed and non-catalyzed reactions was estimated by following the Ozawa method [15-16]. The activation energy values (Table 1) of catalyzed reactions under different conditions unambiguously substantiate the high catalytic activity of BaRuO₃ for carbon / soot oxidation using different feed gas mixtures.

A few mechanisms have been proposed for the catalytic soot/carbon oxidation using oxygen/air. Based on our previous extensive studies on soot oxidation reaction [20-23] as well as the kinetic analysis [24], we postulate that dissociative adsorption of oxygen on catalyst surface followed by its reaction with the solid soot/carbon at the soot-catalyst interface could be the possible mechanism for present perovskite composition. With this background, we have attempted the possibility of explaining high activity in relation to surface structure of this material as derived from crystallographic assumptions. Fig. 3 and Fig. 4 illustrate the possible rich oxygen–ruthenium surface chemistry. The ball model derived in the present study shows abundant population of Ru on –120 planes. We decided to study this plane with the hypothesis of needle particles (crystal growth along c axis), which is classically obtained for hexagonal stacking perovskite. Moreover, in case of BaRuO₃, there is direct Ru-Ru interaction as compared to that of RuO₂, which may favor dissociative adsorption of oxygen. However, another important factor for the relatively higher activity of BaRuO₃ may be the influence of adjacent Ba cation in perovskite structure. The basic character of Ba is expected to weaken the strength of Ru-O bond,
which facilitate the release of adsorbed oxygen. In this way, it is quite possible to explain the excellent catalytic activity of this material, while the material also shows a very important advantage of thermally stabilizing Ru in an oxide matrix.

4. Conclusions

BaRuO$_3$ with perovskite structure can be easily synthesized using co-precipitation method. The catalytic material shows high catalytic activity for soot oxidation reaction as compared to most of the non-PGM (non-platinum group metals) based catalyst reported for direct soot oxidation, while it’s activity is also comparable with PGM metal based catalysts. BaRuO$_3$ shows high soot oxidation activity under both flow type reactor conditions as well as TGA. 120 planes of BaRuO$_3$ are postulated to have abundant Ru atoms, which can facilitate the adsorptive dissociation of oxygen. This surface can also provide weak Ru-O interaction due to the presence of Ba, which may facilitate easy release of dissociated oxygen. It is also significant to achieve high thermal stability for ruthenium in an oxide matrix. The present catalytic studies of BaRuO$_3$ therefore suggest for the preparation of other similar metal ruthenates and study of their detailed catalytic and material properties. This metal ruthenate with perovskite structure shows potential for its applications in environmental catalysis. The high thermal stability of BaRuO$_3$ material is quite striking as this has been a major limitation with Ru based catalytic materials.

Acknowledgements

This work was carried out under the DST-JSPS collaborative research project as well as under the research cooperation between CSIR-NEERI and University of Rennes, France. Thanks are also due to the Director NEERI for providing research facilities.
References


Figures:

Fig. 1: XRD Pattern for BaRuO$_3$

Fig. 2a: Temperature Programmed Oxidation results for carbon oxidation: bare activated carbon

Fig. 2b: Temperature Programmed Oxidation Results for carbon oxidation: activated carbon with BaRuO$_3$ catalyst.

Fig. 3: Ball model of the BaRuO$_3$ (-120) surface

Fig. 4: Projection along [010] of the (-120) surface
Fig. 1
**Fig. 2a & Fig. 2b**
Fig. 3
Fig. 4
Table 1: Activation energy values (Ozawa Plot), kJ/mol

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation Energy kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare carbon black</td>
<td>150 (Air flow) 165 (12% (\text{O}_2)) 160 (12% (\text{O}_2)+10% (\text{CO}_2))</td>
</tr>
<tr>
<td>Carbon black +BaRuO(_3)</td>
<td>120 (Air flow) 135(12% (\text{O}_2)) 130(12% (\text{O}_2)+10% (\text{CO}_2))</td>
</tr>
</tbody>
</table>