NITRIC OXIDE DECOMPOSITION OVER BaRu\textsubscript{x}Bi\textsubscript{1-x}O\textsubscript{3} (X = 0.33, 0.50, 0.67, 1.00) PEROVSKITE-LIKE CATALYSTS

R. Bontchev, K. Cheshkova, D. Mehandjiev* and J. Darriet*
Institute of General and Inorganic Chemistry, 1113 Sofia, Bulgaria.
*Institut de Chimie de la Matiere Condensee de Bordeaux, 33608 Pessac Cedex, France

Received May 30, 1996
In revised form February 18, 1997
Accepted April 16, 1997

Abstract
The catalytic activity of Ba\textsubscript{2}Ru\textsubscript{0.67}Bi\textsubscript{1.33}O\textsubscript{6}, Ba\textsubscript{2}RuBiO\textsubscript{6}, Ba\textsubscript{3}Ru\textsubscript{2}BiO\textsubscript{9} and BaRuO\textsubscript{3} towards NO-decomposition prior to and after treatment with NH\textsubscript{3} has been studied. About 100% degree of conversion has been achieved at 400°C for samples with the highest percentage of hexagonal stacking in their crystal structures. It has been shown that the active sites are units of two or three face-sharing [RuO\textsubscript{6}] octahedra in which a strong Ru-Ru interaction takes place via the common faces.

Keywords: NO decomposition, hexagonal perovskites

INTRODUCTION

A number of ruthenium-containing complex oxides has been studied with respect to their catalytic activity towards NO-reduction [1-6]. Perovskite-like oxides with general formula ARu\textsubscript{x}B\textsubscript{1-x}O\textsubscript{3} (0 < x ≤ 1) where commonly A = Ca, Sr or Ba and B = Rare Earths, Fe, Bi, etc., crystallize in different structural types [1-9]. In pure NO or NO/inert gas mixtures, they show low or no activity [1,2]. At 250-300°C and in the presence of a reducing agent R

*To whom correspondence should be addressed.
(R = CO, H₂) the catalytic activity is high and the proposed mechanism is [1,2]:

\[
M-O-M + R \rightarrow M-\square-M + RO
\]  \hspace{1cm} (1)

\[
M-\square-M + NO \rightarrow M-O-M + Nads
\]  \hspace{1cm} (2)

\[2 \text{Nads} \rightarrow \text{N}_2\] \hspace{1cm} (3)

where M and \(\square\) stand for metals and for oxygen vacancies, respectively.

It has recently been shown that in the Ba-Ru-Bi-O system the increase of ruthenium content leads to an increase of hexagonal stacking in the structure, namely the number of two or three face sharing [RuO₆] octahedra along the c-axis in which a strong metal-metal interaction takes place [7-9]. The aim of our study was to investigate the influence of this effect on the catalytic activity of the series BaRuₓBi₁₋ₓO₃ (x=0.33, 0.50, 0.66, 1.00) towards NO-decomposition, as well as to elucidate the role of the pretreatment with NH₃.

**EXPERIMENTAL**

BaRuO₃, Ba₂Ru₂BiO₉, Ba₂RuBiO₆ and Ba₂Ru₀.₆₇Bi₁.₃₃O₆ were prepared from analytical grade BaCO₃, Bi₂O₃ and RuO₂ using the methods described elsewhere [7-9]. To obtain equivalent surface area of the crystalline powders, the samples were ground in the same manner. The specific surface area of all the samples was estimated by the low temperature adsorption of nitrogen [10] to be 1.8 m² g⁻¹ (±10%).

All the samples prior to and after the catalytic tests were examined by X-ray diffraction, using a DRON-3 diffractometer with Cu- and/or Co-Kα radiation.

Catalytic experiments were carried out in a static vacuum chamber connected with the sampling system of a MX-7303 mass spectrometer. Each sample was examined by a test consisting of the following stages. A. About 0.15 g of a fresh powdered sample was loaded in a holder, put in the chamber and treated at 400°C and total gas pressure of 10⁻³ Torr for 1 h; B. 0.2-0.3 Torr NO was added and the NO/N₂ ratio was monitored by a mass spectrometer as a function of time for 1h; C. After gas evacuation and vacuum treatment at 400°C for 1 h, 0.2-0.3 Torr NH₃ was added for 1h at the same temperature; D. After NH₃ evacuation, stage B was repeated as described above. The degree of conversion \(\eta(\%\) was calculated from the intensities of the mass-peaks 30 (NO) and 28 (N₂).