Retraction for *Catalysis Science & Technology*:

A novel approach for N_2O decomposition over Rh-substituted hexaaluminate catalysts

Rachid Amrousse, Akimasa Tsutsumi and Ahmed Bachar

Catal. Sci. Technol, 2013, **3**, 576–579 (DOI: 10.1039/C2CY20439H). **Retraction published 29 November 2013**

We, the authors, Rachid Amrousse, Akimasa Tsutsumi and Ahmed Bachar, hereby wholly retract this *Catalysis Science & Technology* article. This article has been retracted as it contains significant overlap with the writing in the article, "A novel Ir-hexaaluminate catalyst for N_2O as a propellant", *Chem. Commun*. 2007, 1695–1697, without sufficient attribution to this earlier work being given.

Signed: R Amrousse, A Tsutsumi and A Bachar, November 2013.

This retraction is endorsed by Jamie Humphrey, Managing Editor. Retraction published 29 November 2013.

Catalysis
Science & Technology

RSC Publishing

COMMUNICATION

A novel approach for N_2O decomposition over Rh-substituted hexaaluminate catalysts

Cite this: *Catal. Sci. Technol.*, 2013, **3**, 576

Received 26th June 2012,
Accepted 26th November 2012

DOI: 10.1039/c2cy20439h

www.rsc.org/catalysis

Rachid Amrousse,*[a] Akimasa Tsutsumi[a] and Ahmed Bachar[b]

To develop a novel catalyst for decomposition of N_2O as a green propellant, Rh-substituted hexaaluminate, which can start the N_2O decomposition at 300 °C and can maintain the stability at 1200 °C as adiabatic temperature and with about 200–600 °C as the temperature range for its potential application, has been synthesized for the first time.

Nitrous oxide (N_2O) is a compound that during the last decade has been recognized as a potential contributor to the destruction of the ozone in the stratosphere and acknowledged as a relatively strong greenhouse gas.[1,2] The continuous increase of its concentration, both due to natural and anthropogenic sources (adipic acid production, nitric acid production, fossil fuels and biomass burning) and longer atmospheric residence time (150 years), entails the need to develop efficient catalysts for its decomposition into nitrogen and oxygen. The N_2O catalytic decomposition has been intensively studied over several catalysts.[3–6] However, the catalytic activity towards N_2O decomposition would be significantly affected by various gases that coexist in real exhaust or flue gases. For instance, the presence of excess oxygen is one of the causes for catalyst inhibition.[5] It is essential to synthesize active catalysts for N_2O decomposition at low temperature. For example, spinels,[7–9] ex-hydrotalcites,[10,11] zeolite-based catalysts[12] or alumina supported noble metal (Ir and Rh) catalysts[13,14] are all active at 400 °C for this catalytic decomposition process. Unfortunately, these catalyst series do not survive in high temperature media. Indeed, the total degradation of these samples will be inescapably engendered at above 1200 °C due to structural collapse, phase transformation, sintering phenomena or active phase volatility.

Metal-replaced hexaaluminate substrates are considered as promising materials for high temperature catalytic decomposition.[15–17] It was believed that the high surface area of hexaaluminate supports was necessary to maintain a superior catalytic performance in high temperature catalytic applications above 1200 °C, typically for decomposition of green propellants. Introduction of noble metals into spinel frameworks can enhance the catalytic activity without the decrease of sintering resistance. Unfortunately, few studies have been performed on the reactions other than methane combustion catalyzed by metal-replaced hexaaluminate samples.[18,19]

Based on the exact requirements for N_2O as a propellant, a novel catalyst was developed in the current study by introducing rhodium as an active component into the hexaaluminate structures. Since $Rh/\gamma\text{-}Al_2O_3$ has been reported as a highly active catalyst for N_2O catalytic decomposition,[10] novel Rh-substituted hexaaluminate catalysts were prepared to achieve both goals: high catalytic activity at low temperatures and thermal stability at very high temperatures, which is required for N_2O catalytic reaction.

Pérez-Ramírez and Santiago[20] found that metal-substituted hexaaluminate substrates were used as catalysts for high temperature N_2O abatement. However, they proposed Mn, Fe or Ni transition metals as substitution agents for hexaaluminates which were active only at temperatures higher than 600 °C. Noticeably, such an activity level is too low to be applicable in space propulsion. Therefore, it is essential to synthesize a novel catalyst which can be highly active at low temperatures and stable at high temperatures after N_2O decomposition.

$BaMnAl_{11}O_{19}$ (denoted **BMA** ($x = 0$)) hexaaluminate and Rh substituted hexaalumiante $BaRh_xMn_{1-x}Al_{11}O_{19}$ (denoted **BRMA**), in which $x = 0.3$, 0.5 and 0.8, were synthesized by co-precipitation at 60 °C with $RhCl_3$ as a precursor and $(NH_4)_2CO_3$ as a precipitant. The resultant precipitate was treated at 120 °C for 12 h and calcined at 1200 °C in air for 8 h. For comparison, Rh/BMA and $Rh/\gamma\text{-}Al_2O_3$ were prepared by wet impregnation with a desired amount of $RhCl_3$ to obtain a Rh content of 3 wt%. Finally, the Rh/BMA was calcined at 450 °C for 4 h and $Rh/\gamma\text{-}Al_2O_3$ was calcined at 1200 °C in air for 4 h. N_2O catalytic decomposition processes were performed in a fixed-bed flow reaction system under atmospheric pressure. 200 mg of a catalyst sample was placed in a fritted quartz filter in the half part of the reactor.

---

[a] *JAXA, Japan Aerospace Exploration Agency, 3-1-1 Yoshinoday Chuo-ku, Sagamihara, 252-5210 Kanagawa, Japan. E-mail: rachid.amrousse@jaxa.jp; Fax: +81-42-759-8284; Tel: +81-50-3362-5956*

[b] *Laboratoire des Matériaux Céramiques et Procédés Associés, Université de Valenciennes et du Hainaut-Cambrésis, Valenciennes, France*

Before catalytic tests, the reactor and the catalytic bed were preheated at 400 °C for 2 h using a He + O_2 mixture to remove organic compounds as impurities adsorbed on the catalyst surface, then the temperature was decreased and the gas flow was switched to the reacting gas mixture containing 30 v/v% of the N_2O green propellant in He at a flow rate of 100 mL min^{-1}, corresponding to a gas hour space velocity (GHSV) of 20 000 h^{-1}. The outflowing gas was analyzed by an on-line gas chromatograph (GC-MS-2010 Plus, Shimadzu) equipped with 5 Å molecular sieves and Porapak Q columns, and a TCD detector (SRI 310 CG). The method of mass fragmentation (m/z) was used to identify the nature of each possible ejected gas (*e.g.* N_2O, NO, NO_2, N_2 and O_2 fragments). The N_2O conversions were determined by analyzing N_2O feed concentrations before (bypass) and after passing through the catalyst bed.

Fig. 1 shows the XRD patterns of **BRMA** (x = 0.3, 0.5 and 0.8) samples with different Rh loading (x = 0 to x = 0.8 wt%). For the sample **BMA** (*i.e.* x = 0), well crystallized samples of the (Ba-β-$Al_{12}O_{19}$) phase were observed. When Rh was incorporated into the hexaaluminate phases, there also appears a weak Rh_2O_3 phase as well as the hexaaluminate phase at 2θ = 24° and 47°. The composition of the catalysts was determined by AAS with a WFX-10 atomic absorption spectrometer.

ICP chemical analysis shows that the Rh loading in **BRMA** (x = 0.3) and in Rh/γ-Al_2O_3 was only 2.20 and 1.90 wt%, respectively, both of which were significantly lower than the desired value of 3.00 wt% (the value for the sample calcined at 450 °C), again confirming the evaporation of the Rh component. However, the Rh/γ-Al_2O_3 pattern gives much stronger Rh_2O_3 peaks than **BRMA** (x = 0.3), though the former has a lower Rh loading. This suggests that **BRMA** offers a better metallic accessibility of rhodium by incorporating Rh into the hexaaluminate substrate. The cell parameters listed in Table 1 further confirm that Rh is incorporated into the structure by replacing Al^{3+} cations in $BaAl_{12}O_{19}$. Compared with the a_0 value ($a_0 = b_0$ = 5.576 Å) of $BaAl_{12}O_{19}$, all three **BRMA** samples have a larger a_0 value which increases with the Rh loading, confirming that rhodium cations are located in the hexaaluminate lattice by substituting Al^{3+} cations. However, when the Rh content was increased from x = 0.5 to x = 0.8, a_0 enlargement is almost negligible, implying that only a limited amount of Rh can be incorporated into the structure, and the excess Rh occurs as Rh_2O_3 outside the framework. From Fig. 1 we can also observe that when the Rh content in **BRMA** increased from x = 0.5 to x = 0.8, Rh_2O_3 peaks became strong due to expanded sintering of Rh_2O_3 outside the structure. Moreover, α-alumina and the $BaAl_{12}O_{19}$ spinel phase can be identified alongside the Rh_2O_3 and $BaAl_{12}O_{19}$ hexaaluminate phases. The appearance of the two novel phases further evidenced that excess Rh is not incorporated into the structure.

Table 1 Cell parameters and BET surface areas of prepared hexaaluminate samples

	Cell parameters (Å)		
Sample	$a_0 = b_0$	c_0	SSA (m^2 g^{-1})
BRMA (x = 0.8)	5.598	23.029	16.8
BRMA (x = 0.5)	5.596	22.892	22.3
BRMA (x = 0.3)	5.584	23.322	22.0
$BaAl_{12}O_{19}$	5.576	22.909	24.5
Rh/γ-Al_2O_3	—	—	7.6

From Table 1, we can see that all the hexaaluminate samples have BET surface areas of 16–23 m^2 g^{-1}, larger than that of Rh/γ-Al_2O_3. The large surface area of **BRMA** samples, thanks to their particular sintering resistance, facilitated the metallic accessibility of the active phase, and therefore benefiting the catalytic reaction.

Fig. 2 presents comparison of the catalytic activities of **BMA** (x = 0), Rh/BMA, **BRMA** (x = 0.3, 0.5 and 0.8) and Rh/γ-Al_2O_3 as a function of decomposition temperature.

The **BMA** (x = 0) sample which does not contain Rh did not exhibit activity towards N_2O decomposition below 550 °C. This is in accordance with the results obtained by Pérez-Ramírez and Santiago.[7] When Rh was impregnated into **BMA** (x = 0), the

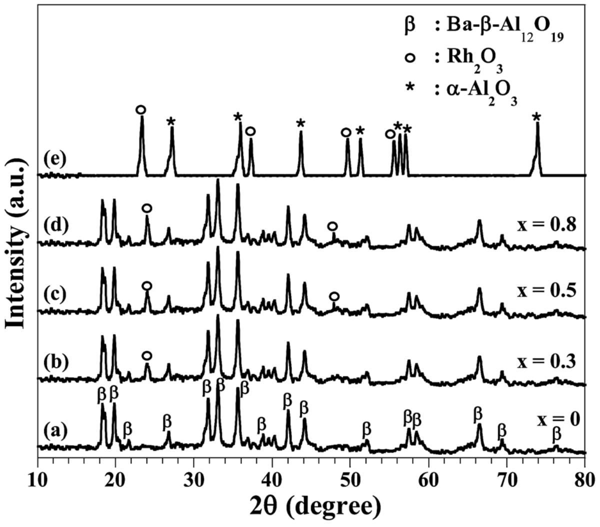

Fig. 1 XRD patterns of (a) **BMA** (x = 0), (b) **BRMA** (x = 0.3), (c) **BRMA** (x = 0.5), (d) **BRMA** (x = 0.8) and (e) Rh/γ-Al_2O_3 samples.

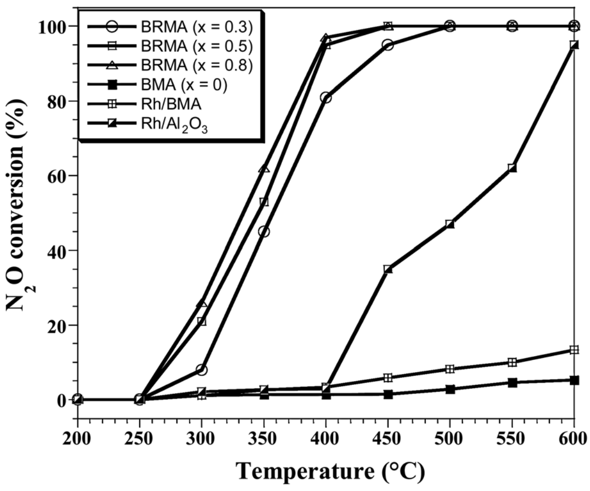

Fig. 2 N_2O catalytic conversion at different temperatures over **BRMA** (x = 0.3; 0.5 and 0.8), Rh/BMA, **BMA** (x = 0) and Rh/γ-Al_2O_3.

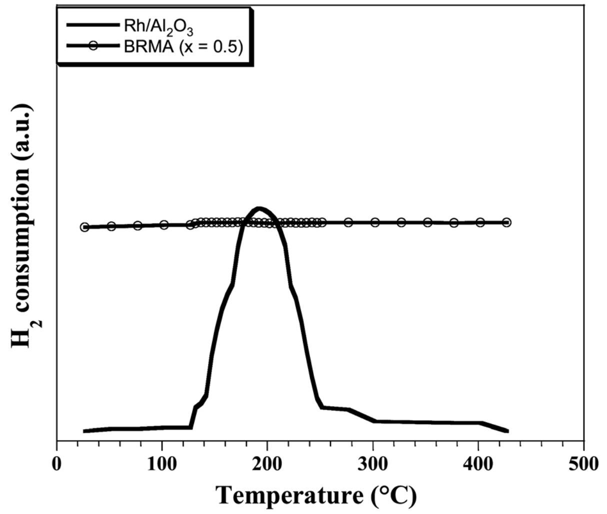

Fig. 3 H_2-TPR profiles of **BRMA** (x = 0.5) and Rh/Al_2O_3 catalysts.

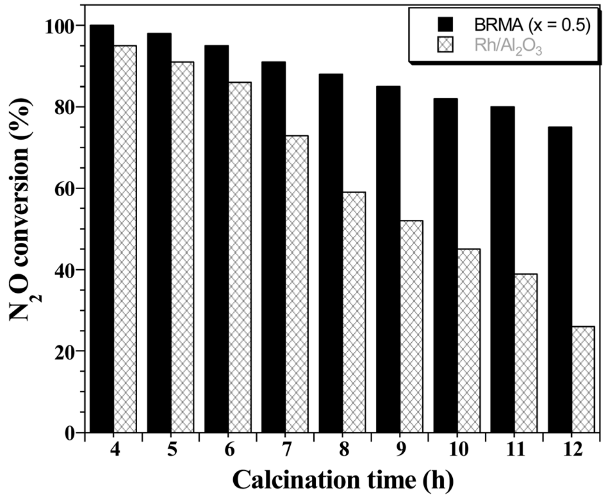

Fig. 4 Effect of calcination time at 1200 °C on catalytic activities of **BRMA** (x = 0.5) and Rh/γ-Al_2O_3 catalysts at 450 °C.

activity was only slightly increased. Significant enhancement in the catalytic activity was observed for the **BRMA** samples. For example, over **BRMA** (x = 0.5), N_2O decomposition started even at about 320 °C and the full N_2O conversion was obtained at 450 °C. Compared with the **BRMA** catalysts, the Rh/γ-Al_2O_3 demonstrated only a moderate activity; complete decomposition of N_2O occurred at 550 °C. It should be pointed out that the BET surface area of Rh/BMA (15 m^2 g^{-1}) was comparable to that of **BRMA** samples (16–23 m^2 g^{-1}). Thus, the lower activity of both Rh/BMA and Rh/γ-Al_2O_3 than that of the **BRMA** samples suggests that the large Rh_2O_3 particles not designated as active sites for the N_2O catalytic decomposition, but rather the active sites were anionic. The same activity of **BRMA** (x = 0.5) and **BRMA** (x = 0.8) samples further confirmed this.

To obtain a clear picture of the catalytic nature of Rh species, the H_2-TPR measurements (Fig. 3) were carried out on **BRMA** (x = 0.5) and Rh/γ-Al_2O_3 samples.

It was found that the Rh species in **BRMA** (x = 0.5) could not be reduced by H_2, which is very different from the case of Rh/γ-Al_2O_3 in which the reduction of Rh supported on alumina started at about 130 °C and reached its maximum at 192 °C. On the other hand, the Rh_2O_3 particles, either on Rh/γ-Al_2O_3 or outside the structure of **BMRA** (x = 0.5), were too large to be able adsorb H_2 molecules. Furthermore, the N_2O decomposition over Rh catalysts can be represented by the anionic redox mechanism initiated by the oxygen-atom transfer with the following principal steps:[21]

$$N_2O_{(g)} + O^{2-}{}_{surf} \rightarrow O_2{}^{2-}{}_{surf} + N_{2(g)}$$

$$\text{(N–O bond breaking } via \text{ } O_2 \text{ transfer)} \qquad (1)$$

$$O_2{}^{2-}{}_{surf} + O_2{}^{2-}{}_{surf} \rightarrow 2O^{2-}{}_{surf} + O_{2(g)}$$

$$(O_2 \text{ recombination}) \qquad (2)$$

In this case, the recombination of $O_2{}^{2-}{}_{surf}$ to produce final $O_{2(g)}$ occurs according to eqn (2). Obviously, some other possible variants of the oxygen migration and recombination steps are also possibly invoking the same species, acting as the active sites for N_2O catalytic decomposition. Clearly, this merits further study.

As noted above, both the initial activity and the thermal stability of the candidate catalyst are very important for decomposition of N_2O as a green propellant. Fig. 4 compares the thermal stabilities of **BMRA** (x = 0.5) and Rh/γ-Al_2O_3.

It can be observed that with the extension of the calcination time at 1200 °C, both catalysts exhibited a decreased activity. However, the activity deterioration over Rh/γ-Al_2O_3 was faster upon extending calcination time. Especially, when the calcination time was extended from 4 to 12 h, N_2O conversion at 450 °C over the Rh/γ-Al_2O_3 catalyst declined from 95 to 26%, whereas it only slightly decreased from 100 to 75% over the **BMRA** (x = 0.5) catalyst, strongly demonstrating the outstanding advantage of **BMRA** (x = 0.5) over Rh/γ-Al_2O_3 in the high temperature reactions. In order to assess the short-term stability of the catalysts, the N_2O catalytic conversion was monitored with time on stream. Other experiments demonstrated that **BMRA** (x = 0.5) could retain 100% N_2O conversion at 450 °C for more than 30 h without any degradation, in contrast with the fast deterioration over the Rh/γ-Al_2O_3 catalyst. Such a deactivation behavior of Rh/γ-Al_2O_3 even at a relatively low reaction temperature of 450 °C may be related to the strong adsorption behavior of the Rh/γ-Al_2O_3 surface towards atomic oxygen generated by N_2O catalytic decomposition. However, in the case of **BMRA** (x = 0.5), Rh was incorporated into the hexaaluminate structure and therefore the interaction between Rh and atomic oxygen could be largely limited. This result further demonstrated that the Rh-replaced hexaaluminate catalysts are highly active and thermally stable catalysts for N_2O decomposition. Moreover, the Rh-substituted hexaaluminate would also offer lower accessibility of Rh for N_2O decomposition which should lead to the lower activity of **BRMA** catalysts.

For space propulsion applications, re-startability is another key parameter to be considered.

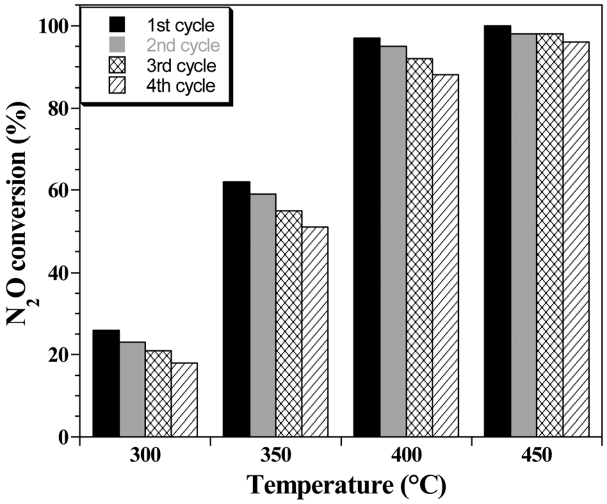

Fig. 5 N_2O catalytic conversions over **BRMA** (x = 0.5) at different temperatures in four cycles of reaction processes.

Fig. 5 shows that the activity only slightly decreased after four reaction cycles due to the loss of catalyst activity from cycle to cycle, demonstrating a good re-startability of the **BRMA** (x = 0.5) catalyst. In conclusion, the current study reveals that Rh-substituted hexaaluminate catalysts can act as encouraging catalysts for high temperature N_2O catalytic decomposition applicable in space propulsion.

Support from Japan Aerospace Exploration Agency (JAXA) for Research Associate Fellowship is gratefully acknowledged.

Notes and references

1 J. C. Kramlich and W. P. Linak, *Prog. Energy Combust. Sci.*, 1994, **20**, 149.

2 M. A. Wojtowicz, J. R. Pels and J. A. Moulijn, *Fuel Process. Technol.*, 1993, **34**, 1.

3 J. Pérez-Ramírez, F. Kapteijn, G. Mul and J. A. Moulijn, *Chem. Commun.*, 2001, 693.

4 G. Centi, A. Galli, B. Montanari, S. Perathoner and A. Vaccari, *Catal. Today*, 1997, **35**, 113.

5 F. Kapteijn, J. Rodriguez-Mirasol and J. A. Moulijn, *Appl. Catal., B*, 1996, **9**, 25.

6 K. Yuzaki, T. Yarimizu, S. Ito and K. Kunimori, *Catal. Lett.*, 1997, **47**, 173.

7 L. Yan, T. Ren, X. L. Wang, D. Ji and J. H. Suo, *Appl. Catal., B*, 2003, **45**, 85.

8 L. Yan, X. M. Zhang, T. Ren, H. P. Zhang, X. L. Wang and J. S. Suo, *Chem. Commun.*, 2002, 860.

9 R. Amrousse and T. Katsumi, *Catal. Commun.*, 2012, **26**, 194.

10 S. Kannan, *Appl. Clay Sci.*, 1998, **13**, 347.

11 L. Obalová, K. Pacultová, J. Balabánová, K. Jirátová, Z. Bastl, M. Valášková, Z. Lacný and F. Kovanda, *Catal. Today*, 2007, **119**, 233.

12 M. Cabrera, F. Kapteijn and J. A. Moulijn, *Chem. Commun.*, 2005, 2178.

13 H. C. Zeng and X. Y. Pang, *Appl. Catal., B*, 1997, **14**, 113.

14 K. Doi, Y. Y. Wu, R. Takeda, A. Matsunami, N. Arai, T. Tagawa and S. Goto, *Appl. Catal., B*, 2001, **35**, 43.

15 M. Machida, K. Eguchi and H. Arai, *J. Catal.*, 1990, **123**, 477.

16 T. Utaka, S. A. Al-Drees, J. Ueda, Y. Iwasa, T. Takeguchi, R. Kikuchi and K. Eguchi, *Appl. Catal., A*, 2003, **247**, 125.

17 G. Groppi, C. Cristiani and P. Forzatti, *Appl. Catal., B*, 2001, **35**, 137.

18 G. Groppi, C. Cristiani and P. Forzatti, *J. Catal.*, 1997, **168**, 95.

19 N. Iyi, S. Takekawa and S. Kimura, *J. Solid State Chem.*, 1989, **83**, 8.

20 M. Santiago and J. Pérez-Ramírez, *Environ. Sci. Technol.*, 2007, **41**, 1704.

21 P. Stelmachowski, F. Zasada, W. Piskorz, A. Kotarba, J. F. Paul and Z. Sojka, *Catal. Today*, 2008, **137**, 423.