COMMUNICATION www.rsc.org/chemcomm | ChemComm

A novel Ir-hexaaluminate catalyst for N_2O as a propellant†

Shaomin Zhu,[ab] Xiaodong Wang,[a] Aiqin Wang,[a] Yu Cong[a] and Tao Zhang*[a]

Received (in Cambridge, UK) 16th February 2007, Accepted 7th March 2007
First published as an Advance Article on the web 28th March 2007
DOI: 10.1039/b702502e

Aiming for designing a novel catalyst for N_2O as a green propellant, Ir-substituted hexaaluminate, which can initiate N_2O decomposition at 623 K and can sustain the stability at 1473 K, has been developed for the first time.

Nitrous oxide (N_2O) has been suggested as an attractive multi-purpose rocket propellant since it can be stored as a liquid and can decompose to N_2 and O_2 exothermically with maximum decomposition temperature of $\sim$1900 K.[1] Preliminary tests have demonstrated that it is feasible to use N_2O as a green monopropellant for small satellite propulsion systems due to system simplicity and low cost associated with the extremely low toxicity, self-pressurizing and compatibility of N_2O with common construction materials.[2,3] However, a stringent challenge is confronted regarding the choice of a suitable catalyst which must be able to initiate the decomposition of N_2O at a low temperature and to survive at very high temperatures.

It is not difficult to find a catalyst to be active enough to initiate the N_2O decomposition at a low temperature. For example, spinels,[4,5] ex-hydrotalcites,[6,7] zeolite-based catalysts[8] or alumina-supported noble metal catalysts[9,10] are all active at $\sim$673 K for this reaction, as extensively reported in the literatures for removing N_2O from exhaust gas. Unfortunately, these catalysts can not survive in a high-temperature environment; severe or even total deactivation will inevitably occur at above 1273 K due to framework collapse, phase transformation, sintering or volatilization of active species.

Metal-substituted hexaaluminates are considered as promising materials for high-temperature catalytic processing.[11–14] These materials have a peculiar layered structure consisting of γ-Al_2O_3 spinel blocks intercalated by mirror planes in which large cations (Ba, La or Sr) are located.[15–17] Introduction of transition or noble metal ions in the spinel blocks can enhance the catalytic activity without decrease of sintering resistance. Associated with their peculiar structure, the metal-substituted hexaaluminates (especially Mn- or Fe-hexaaluminates) exhibited excellent performances in the catalytic combustion of methane.[12,13] However, few studies have been made on the reactions other than methane combustion catalyzed by metal-substituted hexaaluminates.

Based on the stringent requirements for N_2O as a propellant, we designed a novel catalyst in the present work by introducing iridium as an active component into the framework of hexaaluminates. Since Ir/Al_2O_3 has been reported as a highly active catalyst for N_2O decomposition,[1] our designed Ir-substituted hexaaluminates will be expected to be both active at a low temperature and thermally stable at a very high temperature, which is required for N_2O as a propellant. During our preparation of this paper, we read a very recently published work by Pérez-Ramírez and Santiago,[18] in which metal-substituted hexaaluminates were employed as catalysts for high-temperature N_2O abatement in the chemical industry. However, they used Mn, Fe or Ni-substituted hexaaluminates which were only active at temperatures as high as >873 K. Obviously, such an activity level is too low to be applicable in propulsion systems. It is, therefore, necessary to develop a new catalyst which can be highly active at low temperatures and stable enough at very high temperatures for N_2O as a green propellant.

$BaFeAl_{11}O_{19-\alpha}$ (denoted as BFA) hexaaluminate and Ir-substituted hexaaluminate ($BaIr_xFe_{1-x}Al_{11}O_{19-\alpha}$ (x = 0.2, 0.5, 0.8), denoted as BIFA) were prepared by co-precipitation[14] at 333 K with metal nitrates and H_2IrCl_6 as precursors and $(NH_4)_2CO_3$ as a precipitant. The resultant precipitate was dried at 393 K for 12 h and calcined at 1473 K in air for 4–10 h. For comparison, Ir/BFA and Ir/Al_2O_3 were prepared by impregnation with a desired amount of H_2IrCl_6 to give an Ir loading of 5 wt%. Finally, the Ir/BFA was calcined at 773 K for 2 h and Ir/γ-Al_2O_3 was calcined at 1473 K in air for 4 h. Catalytic decomposition of N_2O was carried out in a fixed-bed flow reaction system under atmospheric pressure. 100 mg of a catalyst sample was placed on a quartz filter in the middle part of the reactor. Prior to the reaction, the catalyst sample was pre-reduced with pure H_2 at 673 K for 2 h. After cooling to room temperature in Ar, the gas flow was switched to the reacting gas mixture containing N_2O (30 v/v%) in Ar at a flow rate of 50 ml min^{-1}, corresponding to a gas hour space velocity (GHSV) of 30 000 ml g^{-1} h^{-1}. The effluent gas was analyzed on-line by an Agilent 6890 N gas chromatograph equipped with Chromosorb 103 and Porapak Q columns. N_2O conversions were monitored either with the reaction temperature or with the time on stream.

Fig. 1 shows the XRD patterns of the BIFA and Ir/Al_2O_3 samples with different Ir contents. For the sample BFA (*i.e.* $x = 0$), we can only observe the well crystallized hexaaluminate ($BaAl_{12}O_{19}$) phase. When Ir was incorporated into the hexaaluminate (x = 0.2 and 0.5), there also appears a very weak IrO_2 phase besides the hexaaluminate phase. A detailed XRD examination (Fig. S1, ESI†) on both the BIFA sample (x = 0.2) and Ir/Al_2O_3 sample which had been calcined at different temperatures reveals that most of the Ir component in the two samples has been volatilized when the calcination temperature attained 1473 K. ICP analysis shows that the Ir content in the

---

[a] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, PO Box 110, Dalian, 116023, P. R. China. E-mail: Taozhang@dicp.ac.cn; Fax: +86-411-84691570; Tel: +86-411-84379015*
[b] *Graduate University of Chinese Academy of Sciences, Beijing, 100049, P. R. China*

† Electronic supplementary information (ESI) available: XRD and H_2-TPR patterns of BIFA (x = 0.2) and Ir/Al_2O_3 catalysts calcined at different temperatures. See DOI: 10.1039/b702502e

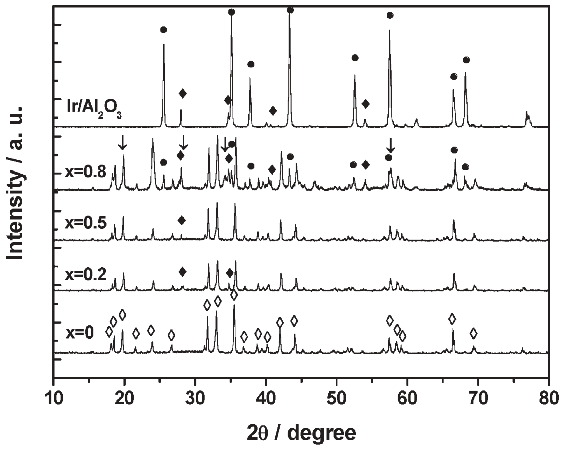

Fig. 1 X-Ray diffraction patterns for $BaIr_xFe_{1-x}Al_{11}O_{19-\alpha}$ and Ir/Al_2O_3 catalysts: (◇) IrO_2, (◆) $BaAl_{12}O_{19}$, (●) α-Al_2O_3, (↓) $BaAl_2O_4$.

BIFA ($x = 0.2$) and in the Ir/Al_2O_3 was only 1.92 and 1.40 wt%, respectively, both of which were significantly lower than the initial value of 5.00 wt% (the value for the sample calcined at 773 K), again confirming the evaporation of the Ir component. However, it is noted from Fig. 1 that the Ir/Al_2O_3 gives much stronger IrO_2 peaks than the BIFA ($x = 0.2$), though the former has a lower Ir content. This suggests that the BIFA offers a better dispersion of iridium by incorporating Ir into the hexaaluminate structure. The cell parameters listed in Table 1 further confirm that Ir is incorporated into the framework by substituting Al^{3+} cations in the $BaAl_{12}O_{19-\alpha}$. Comparing with the a_0 value ($a_0 = b_0 = 5.576$ Å) of the $BaAl_{12}O_{19-\alpha}$, all the three BIFA samples have a larger a_0 value which increases with the Ir content, confirming that iridium cations are located in the hexaaluminate lattice by replacing Al^{3+} cations. However, when Ir content was increased from $x = 0.5$ to $x = 0.8$, the enlargement of the a_0 value is almost negligible, implying only a very limited amount of Ir can be incorporated into the framework, and the excess Ir occurs as IrO_2 out of the framework. From Fig. 1, we can also see that when the Ir content in the BIFA increased from $x = 0.5$ to $x = 0.8$, IrO_2 peaks became strong due to the extensive sintering of the IrO_2 out of the framework. In addition, both α-Al_2O_3 and $BaAl_2O_4$ spinel phase can be identified besides the IrO_2 and $BaAl_{12}O_{19}$ hexaaluminate phase. The appearance of the two new phases further evidenced that the excess part of Ir is not incorporated into the framework. From Table 1, we can see all the hexaaluminate samples have BET surface areas of 15–25 $m^2\ g^{-1}$, four times larger than that of Ir/Al_2O_3. The large surface area of the BIFA, thanks to its particular sintering-resistance, facilitated the dispersion of the active component, and therefore benefiting the catalytic reaction.

Table 1 Cell parameters and BET surface areas of $BaIr_xFe_{1-x}Al_{11}O_{19-\alpha}$ and $BaAl_{12}O_{19-\alpha}$

	Cell parameters/Å		
Sample	$a_0 = b_0$	c_0	$S_{BET}/m^2\ g^{-1}$
$BaIr_{0.8}Fe_{0.2}Al_{11}O_{19-\alpha}$	5.598	23.029	17.2
$BaIr_{0.5}Fe_{0.5}Al_{11}O_{19-\alpha}$	5.596	22.892	21.8
$BaIr_{0.2}Fe_{0.8}Al_{11}O_{19-\alpha}$	5.582	23.166	23.2
$BaAl_{12}O_{19-\alpha}$	5.576	22.909	24.5
Ir/Al_2O_3	—	—	6.4

Fig. 2 compares the catalytic activities of the BFA, Ir/BFA, BIFA and Ir/Al_2O_3 as a function of reaction temperature. The BFA sample which does not contain Ir did not exhibit activity towards N_2O decomposition until 823 K. This is in accordance with the results obtained by Pérez-Ramírez and Santiago.[18] When Ir was impregnated onto the BFA, the activity was only slightly increased. Significant enhancement in the catalytic activity was observed on the BIFA samples. For example, over the $BaIr_{0.5}Fe_{0.5}Al_{11}O_{19-\alpha}$, N_2O decomposition started even at about 600 K and the full N_2O conversion was obtained at 723 K. Comparing with the BIFA catalysts, the Ir/Al_2O_3 demonstrated only a moderate activity; complete decomposition of N_2O occurred at 823 K. It should be pointed out that the BET surface area of Ir/BFA (14.8 $m^2\ g^{-1}$) is comparable to that of the BIFA samples (17.2–23.2 $m^2\ g^{-1}$). Thus, the lower activity of both Ir/BFA and Ir/Al_2O_3 than that of the BIFA samples suggests that the large IrO_2 particles are less active than the framework Ir species. The same activity of the $BaIr_{0.5}Fe_{0.5}Al_{11}O_{19-\alpha}$ and $BaIr_{0.8}Fe_{0.2}Al_{11}O_{19-\alpha}$ samples further confirmed this. To obtain a clear picture on the catalytic nature of framework Ir species, both H_2-TPR (Fig. S2, ESI†) and CO-chemisorption were performed on the BIFA and Ir/Al_2O_3 samples. It was found that the framework Ir species in the BIFA could not be reduced by H_2, which is very different from the case of Ir/Al_2O_3. On the other hand, the IrO_2 particles, either on the Ir/Al_2O_3 or outside the framework of BIFA, were too large to be able to adsorb CO molecules. These experimental results demonstrate that the framework Ir species, acting as the active sites for N_2O decomposition, has a special structure which is different from that on the Ir/Al_2O_3. Certainly, this is worthwhile for further study.

As we emphasized above, both the initial activity and the thermal stability of the catalyst are very important for N_2O as a propellant. Fig. 3 compares the thermal stabilities of BIFA and Ir/Al_2O_3. It can be seen from Fig. 3(a) that with the prolonging of the calcination time at 1473 K, both catalysts exhibited a decreased activity. However, the activity decay over the Ir/Al_2O_3 was more rapid upon extending of calcination time. In particular, when the calcination time was prolonged from 4 to 10 h, N_2O conversion at 773 K over the Ir/Al_2O_3 catalyst declined from 89 to 3.3%, whereas it only slightly decreased from 100 to 78% over the BIFA catalyst, strongly demonstrating the outstanding advantage of the IBFA

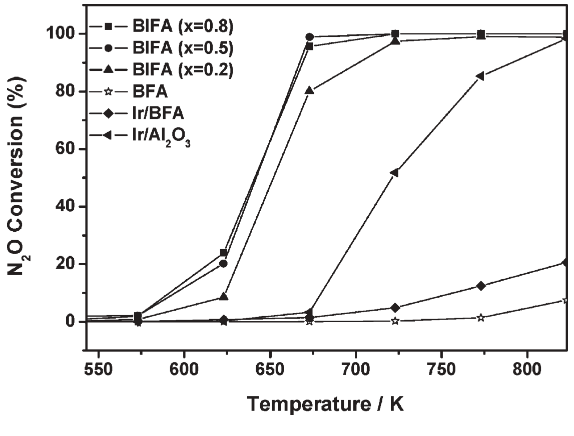

Fig. 2 N_2O conversion as a function of reaction temperature over $BaIr_xFe_{1-x}Al_{11}O_{19-\alpha}$, Ir/BFA, BFA and Ir/Al_2O_3 catalysts.

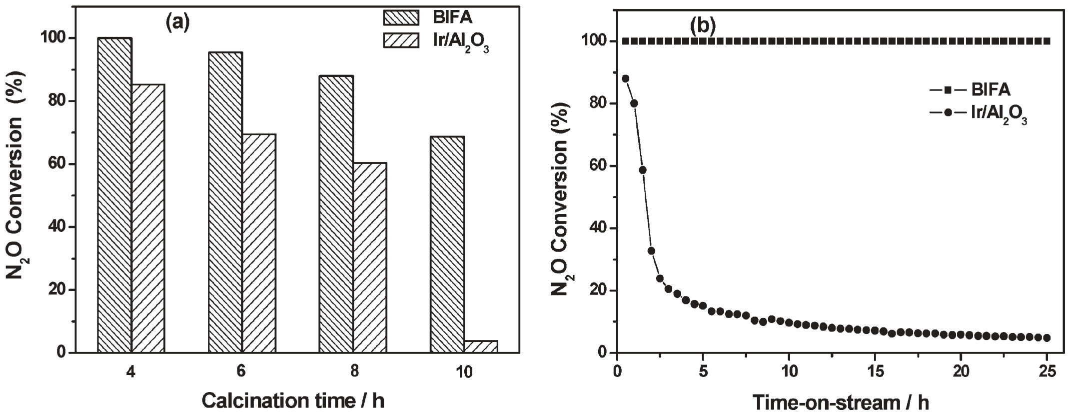

Fig. 3 (a) Effect of calcination time at 1473 K on catalytic activities of BIFA and Ir/Al_2O_3 catalysts at 773 K. (b) Evolution of N_2O conversions at 773 K as a function of the time-on-stream over BIFA and Ir/Al_2O_3 catalysts.

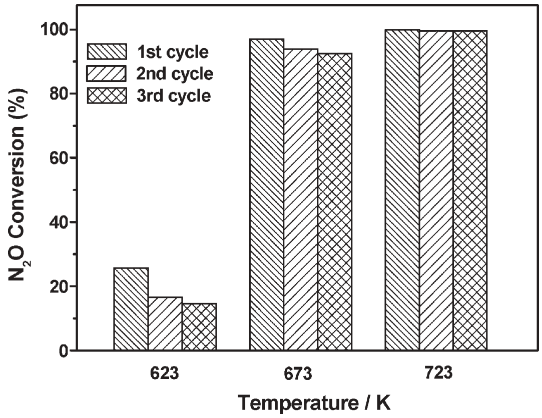

Fig. 4 N_2O conversions over $BaIr_{0.8}Fe_{0.2}Al_{11}O_{19-\alpha}$ at varying reaction temperatures in three cycles of reaction.

over Ir/Al_2O_3 in the high-temperature reactions. In order to assess the short-term stability of the catalysts, the N_2O conversion was monitored with time on stream. As illustrated in Fig. 3(b), BIFA could retain 100% N_2O conversion at 773 K for more than 26 h without any decay, in contrast with the rapid decay over the Ir/Al_2O_3. Such a deactivation behaviour of the Ir/Al_2O_3 even at relatively low reaction temperature of 773 K may be related with the strong adsorption of the Ir/Al_2O_3 surface towards atomic oxygen generated by N_2O decomposition.[19,20] However, in the case of the BIFA, Ir was incorporated into the framework of the hexaaluminate and therefore the interaction between Ir and atomic oxygen could be largely limited. This result further demonstrated that the Ir-substituted hexaaluminates are highly active and thermally stable catalysts for N_2O decomposition.

For application in spacecraft propulsion systems, re-startability is another key parameter to be considered. Fig. 4 shows that the activity only slightly decreased after three reaction cycles, demonstrating a good re-startability of the BIFA catalysts.

In summary, our present work has demonstrated that Ir-substituted hexaaluminates can be act as promising catalysts for high concentration N_2O decomposition applicable in propulsion systems.

Support from the National Science Foundation of China (NSFC) for Distinguished Young Scholars (No. 20325620) and NSFC grant (No. 20673116) are gratefully acknowledged.

Notes and references

1 J. R. Wallbank, P. A. Sermon, A. M. Baker, L. Courtney and R. M. Sambrook, *The 2nd International Conference on Green Propellants for Space Propulsion*, Italy, 7–8 June 2004.
2 V. Zakirov, V. Goeman, T. J. Lawrence and M. N. Sweeting, *Proceedings of the 14th Annual AIAA/USU Conference on Small Satellites*, USA, 21–24 August 2000.
3 V. Zakirov, T. J. Lawrence, J. J. Sellers and M. N. Sweeting, *Proceedings of the 51st International Astronautical Congress*, Rio de Janeiro, Brazil, 2–6 October 2000.
4 L. Yan, T. Ren, X. L. Wang, D. Ji and J. H. Suo, *Appl. Catal., B*, 2003, **45**, 85.
5 L. Yan, X. M. Zhang, T. Ren, H. P. Zhang, X. L. Wang and J. S. Suo, *Chem. Commun.*, 2002, 860.
6 S. Kannan, *Appl. Clay Sci.*, 1998, **13**, 347.
7 L. Obalova’, K. Pacultova’, J. Balaba’nova’, K. Jira’tova’, Z. Bastl, M. Vala’sškova’, Z. Lacny’ and F. Kovanda, *Catal. Today*, 2007, **119**, 233.
8 M. Cabrera, F. Kapteijn and J. A. Moulijn, *Chem. Commun.*, 2005, 2178.
9 H. C. Zeng and X. Y. Pang, *Appl. Catal., B*, 1997, **14**, 113.
10 K. Doi, Y. Y. Wu, R. Takeda, A. Matsunami, N. Arai, T. Tagawa and S. Goto, *Appl. Catal., B*, 2001, **35**, 43.
11 M. Machida, K. Eguchi and H. Arai, *J. Catal.*, 1990, **123**, 477.
12 T. Utaka, S. A. Al-Drees, J. Ueda, Y. Iwasa, T. Takeguchi, R. Kikuchi and K. Eguchi, *Appl. Catal., A*, 2003, **247**, 125.
13 G. Groppi, C. Cristiani and P. Forzatti, *Appl. Catal., B*, 2001, **35**, 137.
14 G. Groppi, C. Cristiani and P. Forzatti, *J. Catal.*, 1997, **168**, 95.
15 N. Iyi, S. Takekawa and S. Kimura, *J. Solid State Chem.*, 1989, **83**, 8.
16 A. J. Zarur and J. Y. Ying, *Nature*, 2000, **403**, 65.
17 A. J. Zarur, N. Z. Mehenti, A. T. Heibel and J. Y. Ying, *Langmuir*, 2000, **16**, 9168.
18 J. P. Ramírez and M. Santiago, *Chem. Commun.*, 2007, 619.
19 S. Tanaka, K. Yuzaki, S. Ito, H. Uetsuka1, S. Kameoka and K. Kunimori, *Catal. Today*, 2000, **63**, 413.
20 V. Boissel, S. Tahir and C. A. Koh, *Appl. Catal., B*, 2006, **64**, 234.