

SUPERIOR PERFORMANCE OF IRIIDIUM- HEXAALUMINATE CATALYSTS FOR NITROUS OXIDE DECOMPOSITION

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ABSTRACT

Catalytic decomposition of nitrous oxide (N_2O) can be potentially applied to small satellite propulsion systems due to system simplicity and low cost associated with the non-toxicity, self-pressurizing and compatibility of N_2O with common construction materials. Ir/ Al_2O_3 (Shell 405) has been reported to be one of the most active catalysts towards the decomposition of N_2O . However, the high temperature attained during the decomposition of N_2O would lead to drastic loss in activity of the Ir/ Al_2O_3 due to sintering and evaporation of active Ir species. Therefore, maintaining the stability of the catalyst at high temperatures will become the major challenge for application of N_2O as a propellant. Hexaaluminate is a promising material showing superior resistance to sintering at high temperatures. In this work, we for the first time introduced Ir species into hexaaluminate by co-precipitation, and found that Ir-hexaaluminate catalysts exhibited excellent activity and superior stability against high-temperature deactivation for N_2O decomposition, which would be more promising for resolving the challenges of activity and stability of catalyst under high temperatures.

1. INTRODUCTION

In recent years, N_2O has been extensively studied as an attractive rocket propellant for its superior properties. First, it is non-toxic, therefore it could be handled with minimal safety equipment. Second, it is a kind of liquefied gas. At 20°C its saturated vapor pressure reaches 52 bar, while at 30°C it comes to 63 bar. Such high saturated vapor pressure enables N_2O to self-sustain the feed in the form of gas or liquid and to pressure other liquid fuel, which provides the possibility for the propulsion system to miniaturize. Third, it can be extended to three-mode propulsions. High saturated vapor pressure could make nitrous oxide gas used as cold-gas directly, which would provide power for attitude control of the spacecraft. Exothermically decomposition property makes nitrous oxide used as monopropellant, and this could provide thrust for spacecraft station-keeping and small orbit maneuvers. Meanwhile, when nitrous oxide decomposes, high

temperature oxygen is generated, which supports combustion with many kinds of fuels and could form hybrid bipropellant system for the large orbital maneuvering. In general, nitrous oxide propulsion has the advantages of covering the whole range of propulsion functions for small satellites and simplifying the multi-mode propulsion systems with one self-pressurizing propellant. N_2O is a potential substitute for toxic hydrazine monopropellant.

In Britain, nitrous oxide has been successfully tested within a resistojet propulsion system aboard UoSAT-12. It contained 2.1 kg of nitrous oxide which was sufficient for 14h of resistojet propulsion. In America, Scaled Composites has used nitrous oxide as the oxidizer for the hybrid engine powering "SpaceshipOne" for more than a minute to the altitude of 100 Km, and won the Ansari X-Prize in 2004. While in China, nitrous oxide propulsion has also drawn a lot of attention and many fundamental as well as applied studies have been carried out.

N_2O is stable and comparatively unreactive at ordinary temperatures. Its bimolecular decomposition only takes place at above 520 °C with activation energy of about 250 kJ/mol. Therefore, decomposition catalysts are required to lower the decomposition temperature as well as to accelerate the decomposition reaction. It has been testified that catalytic decomposition is a key process for nitrous oxide mono- and bi- propulsions.

University of Surrey and Surrey Satellite Technology Ltd (Limited) did a lot of research studies on N_2O decomposition catalysts, and many catalytic systems have been tested with various equipments. But up to the present, stable catalysts to endure the high temperature of the order 1100-1600°C generated from N_2O decomposition are still main challenge. Precious metal catalysts such as Ir/ Al_2O_3 (Shell 405) and Rh based catalysts are reported to have high activity towards this reaction. However, when the temperature was risen to above 1473K, Ir-IrO₂ shows signs of sintering first and then begins to volatilize gradually. At the same time, alumina begins to irreversibly convert to α - Al_2O_3 . And upon calcination at 1873K, only traces of retained Ir are remained in the catalyst [1].

Hexaaluminate related compound is a promising heat resisted material. It has the peculiar layered spinel structure, which is composed of closely spaced spinel blocks separated by mirror planes, allows retain the moderate surface area at high temperatures [2-6]. Catalytically active components can be substituted into the structure to form a highly dispersed catalyst system, which favors the saving of active component at high temperature [2]. Therefore, the combining of the special hexaaluminate structure and precious metal Ir provides the potential of designing an active and thermal-resistant catalyst towards nitrous oxide decomposition. In this work, we for the first time designed a novel catalyst via introducing Ir into the hexaaluminate structure in one-pot preparation procedure.

2. EXPERIMENTAL

Ir-hexaaluminate ($\text{Ir}_x\text{BaFe}_{1-x}\text{Al}_{11}\text{O}_{19}$, denoted as IBFA- y , y indicates calcination temperature) was prepared by co-precipitation method at 60°C with metal nitrates (except for H_2IrCl_6) as precursors and $(\text{NH}_4)_2\text{CO}_3$ as a precipitant [7-8]. After filtration, washing and drying at 110°C , the solid product was calcined at 500°C for 2h followed by calcination at 1200°C for 2h, 4h, 6h and 10h. For comparison, $\text{Ir-Al}_2\text{O}_3$ catalysts were also prepared and subjected to the same Iridium content.

Nitrous oxide decomposition reactions were performed on a micro-reactor using GC on-line analysis. 100 mg catalyst sample together with inert quartz was used with a total space velocity of 30000h^{-1} , and the feed gas was diluted with 70% balanced Ar (argon). If not specially illustrated, catalysts are all pretreated with H_2 for 2h at 400°C .

SEM, BET, XRD and TPR techniques were also tested to characterize the samples.

3. RESULTS AND DISCUSSION

The structure of IBFA-1200 has been characterized by SEM (Figure 1). The morphology of the obtained $\text{Ir-Al}_2\text{O}_3$ -1200 particle was a $0.1\mu\text{m}$ sized pellet, while the IBFA-1200 showed a very uniform plate-like morphology. Anisotropic crystal growth occurred to IBFA-1200.

XRD was used to characterize the structure of $\text{Ir-Al}_2\text{O}_3$ and Ir-hexaaluminate via calcination temperature (Figure 2). After calcination 2h at 500°C , both catalysts displayed almost the same IrO_2 diffraction peaks only. Besides, all the samples showed high surface areas of about $240\text{-}280\text{ m}^2/\text{g}$, which indicated the presence of amorphous compounds along with the above crystalline

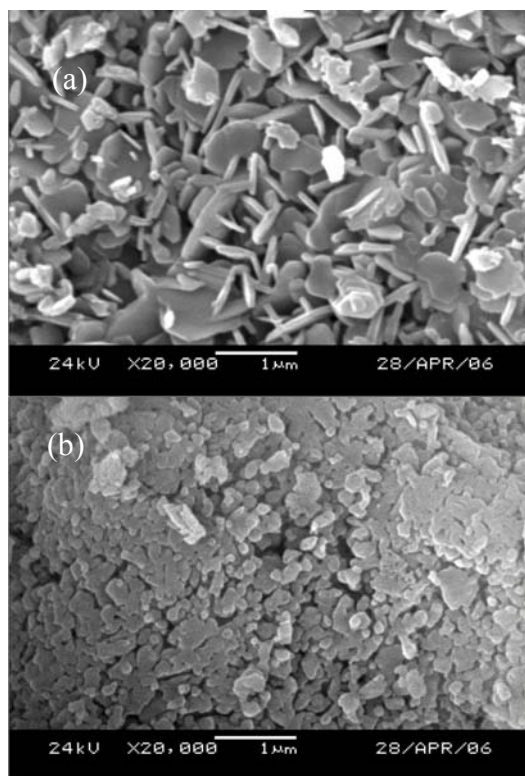


Figure 1. SEM morphology of (a) IBFA-1200 and (b) $\text{Ir-Al}_2\text{O}_3$ -1200.

phases. Differences in phase composition became obvious when the samples were calcined at 1200°C . $\alpha\text{-Al}_2\text{O}_3$ phase was formed in $\text{Ir-Al}_2\text{O}_3$, and the conversion of alumina crystal led to a drastic loss in surface area ($6\text{ m}^2/\text{g}$). In contrast, mixed oxide sample transformed to hexaaluminate structure in stead, accompanied with a small amount of BaAl_2O_4 spinel phase. At the same time, trace IrO_2 phase was still detected. The BET surface area was measured to be 4 times higher than that of $\text{Ir-Al}_2\text{O}_3$. From these results it can be supposed that the formation of hexaaluminate is the reason of preventing the surface diffusion of alumina, and inhibiting the sintering of the sample.

TPR technique was applied to probe into the state of iridium (Figure 3). Two reduction peaks centered at 140°C and 220°C were detected in moderate calcination samples. They were ascribed to the highly dispersed surface iridium and bulk crystal iridium, respectively. However, when the samples were calcined at high temperature, the low temperature reduction peaks disappeared, and the high temperature reduction peaks became larger and broader, and they intended to move towards higher temperature. Meanwhile, a new shoulder peak at 250°C appeared in the mixed oxide sample. These results suggested that after calcination at 1200°C , the surface iridium species agglomerate to more huge clusters, and some iridium incorporate into the

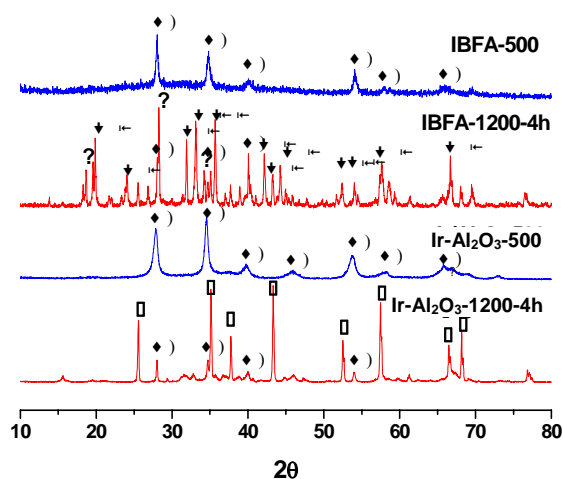


Figure 2. X-ray diffraction patterns of IBFA and Ir-Al₂O₃ after calcination at (a) 500 °C and (b) 1200 °C respectively.

hexaaluminate structure with the formation of hexaaluminate phase, which leads to the shoulder peak of IBFA-1200.

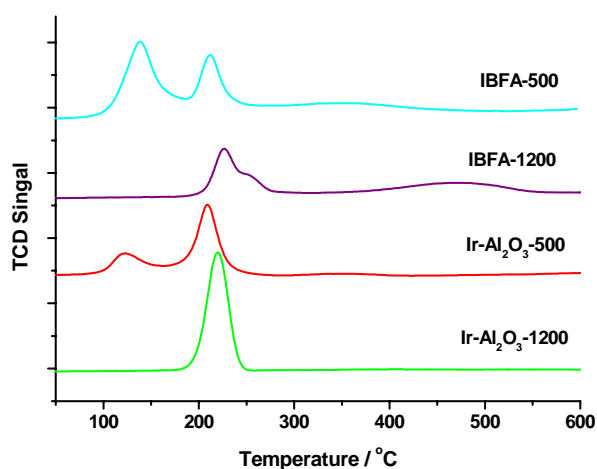


Figure 3. H₂-TPR profiles of IBFA and Ir-Al₂O₃ calcined at different temperatures.

A comparison test between IBFA and Ir-Al₂O₃ (Figure 4) showed that Ir-hexaaluminate exhibited very high activity after calcination 2h at 1200 °C (Figure 4). It exhibited almost similar activity to that after moderate calcinations. However, Ir-Al₂O₃ demonstrated fairly low activity. Correlating to the TPR results, it could be deduced that the highly dispersed surface iridium accounts for the high activity of the low calcination sample, and the incorporated iridium in the

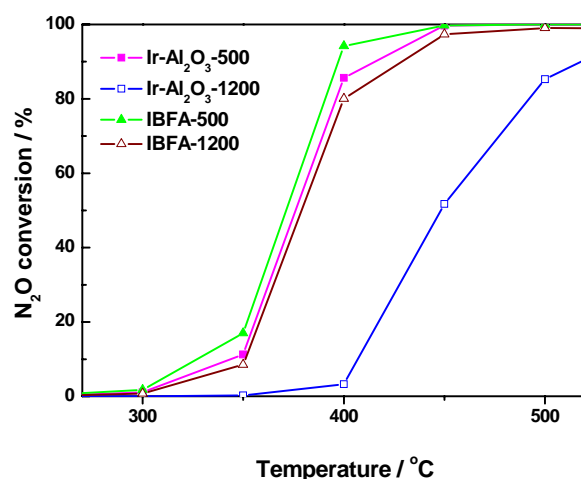


Figure 4. Catalytic performances of Ir-Al₂O₃ and IBFA calcined 4h at different temperatures.

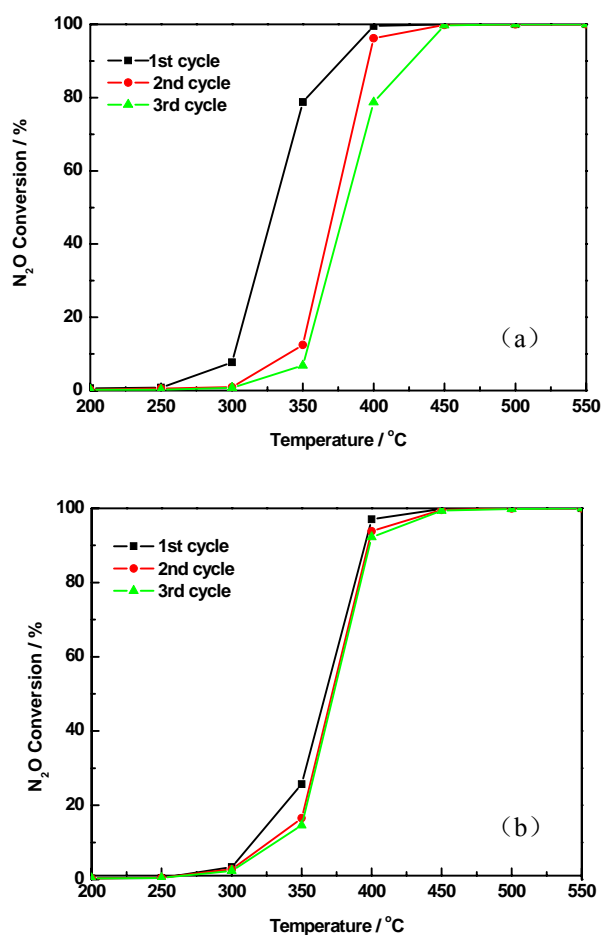


Figure 5. Restart performances of IBFA calcined at (a) 500 °C and (b) 1200 °C.

hexaaluminate structure is responsible for that after high temperature calcination. Bulk iridium crystals do not favor nitrous oxide decomposition.

As an important parameter of monopropellant, the restart stability was tested in this work. As shown in Figure 5, good activities were remained on the catalysts calcined at 1200 °C, while when the samples were calcined at moderate temperature, the conversion decreased with the running cycle. This suggested that stable hexaaluminate structure is crucial to nitrous oxide decomposition.

The results on calcination time (Figure 6) further illustrated that Ir-hexaaluminate has stable structure, and they can well sustain the catalytic activity compared to that of Ir-Al₂O₃. However, too long-time calcination led to the decrease of catalytic activity to a certain degree.

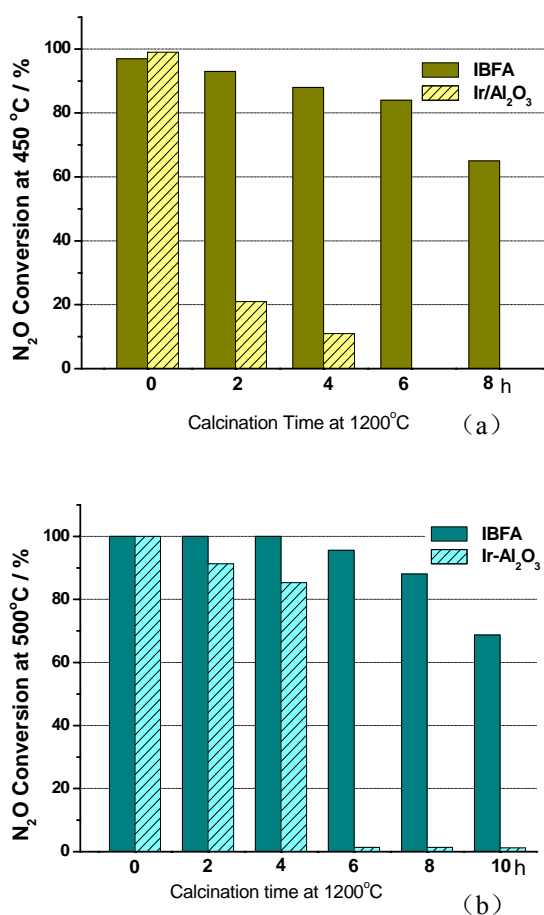


Figure 6. Effect of calcination time at 1200 °C on the catalytic activities of (a) 450 °C and (b) 500 °C over IBFA and Ir-Al₂O₃ catalyst.

It was worth noting that pre-reduction with H₂ for IBFA-1200 induced high activity, whereas pretreatment with O₂ resulted in very poor performance (Figure 7). Considering that N₂O decomposition produces an oxidizing atmosphere, we postulated that free oxygen in the pretreatment atmosphere plays completely different role to the produced oxygen, and the reduction with H₂ not only creates active center in the form of metallic Ir, but also induces the redistribution of active Ir species.

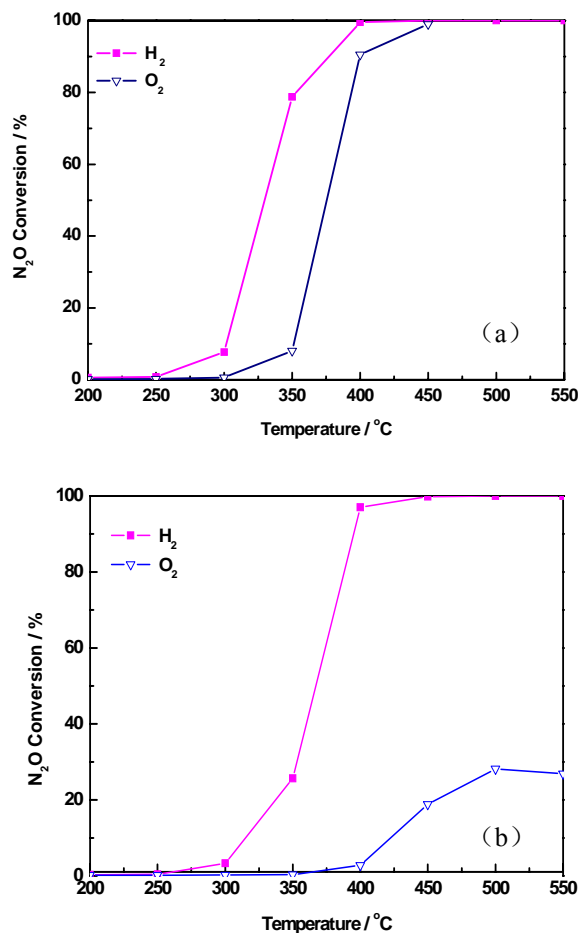


Figure 7. Effect of pretreatment condition for (a) IBFA-500 and (b) IBFA-1200 °C.

To further shed light on the nature of active Ir species in the Ir-hexaaluminate catalysts, catalytic reactions were performed on the samples prepared with different methods (Figure 8). Iridium impregnated on hexaaluminate exhibited very low activity in contrast to Ir-hexaaluminate. This gives more evidences that the incorporated iridium in the hexaaluminate structure is the active origin for catalyst calcined at high temperatures.

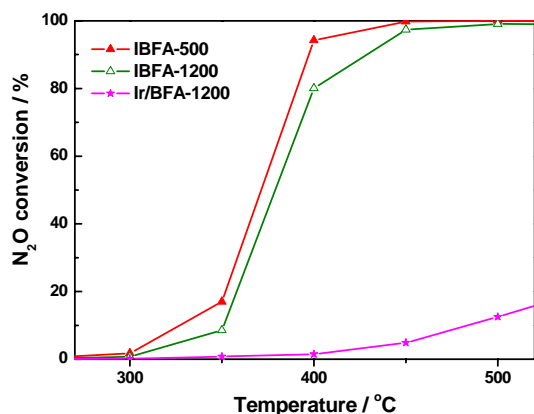


Figure 8. Comparison of preparation method.

4. CONCLUSION

Ir-haxaaluminate is a promising catalyst toward nitrous oxide decomposition. It showed much higher activity than that of Ir-Al₂O₃ after calcination at 1200 °C, and it exhibited good thermal stability. The reduced iridium incorporated in the hexaaluminate structure is supposed to be the active center for catalyst calcined at high temperature.

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