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## Communication

# Superior performance of iridium supported on rutile titania for the catalytic decomposition of N<sub>2</sub>O propellants

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## ARTICLE INFO

## Article history:

Received 12 March 2018

Accepted 9 April 2018

Published 5 July 2018

## Keywords:

Heterogeneous catalysis

Nitrous oxide

Catalytic decomposition

Iridium catalyst

Titania

## ABSTRACT

N<sub>2</sub>O is a promising green propellant and exhibits great potential for satellite propulsion systems. It is difficult for catalytic decomposition, which is an important way to initiate the propulsion process, to occur at temperatures below 600 °C due to the high activation energy of N<sub>2</sub>O. In this work, we report an Ir supported on rutile TiO<sub>2</sub> (Ir/r-TiO<sub>2</sub>) catalyst which exhibits a fairly high activity for high-concentration N<sub>2</sub>O decomposition. HAADF-STEM, H<sub>2</sub>-TPR, and XPS results indicate that highly dispersed Ir particles and improved oxygen mobility on the Ir/r-TiO<sub>2</sub> could facilitate the decomposition of N<sub>2</sub>O and desorption of the adsorbed oxygen. Bridge-bonded peroxide intermediates were observed with *in-situ* DRIFT and herein, a detailed decomposition route is proposed.

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Nitrous oxide (N<sub>2</sub>O) is a promising green propellant for small satellites because of its many advantages, such as system simplicity, multiple propulsion modes, extremely low toxicity, and compatibility with common construction materials. The direct decomposition of N<sub>2</sub>O to N<sub>2</sub> and O<sub>2</sub> is the most effective method for propulsion applications. However, although this process is thermodynamically favorable, it does not readily occur at temperatures below 600 °C due to its high activation energy of about 250 kJ mol<sup>-1</sup> [1]. This energy requirement cannot be satisfied by the energy supply systems of small satellites. Therefore, there is an urgent need to develop appropriate decomposition catalysts with high activity at low temperatures as well as good stability at high temperatures.

A wide variety of catalysts have been developed for the di-

rect decomposition of N<sub>2</sub>O, *e.g.* pure and mixed oxides, transition metal-exchanged zeolites, and supported metal catalysts [2–4]. For example, a cobalt spinel catalyst which was promoted by cerium exhibited a high activity for N<sub>2</sub>O decomposition, completely decomposing N<sub>2</sub>O at a temperature below 200 °C [5]. The Fe-ZSM catalyst was highly active and stable for the removal of N<sub>2</sub>O in simulated tail-gas from nitric acid plants [6]. Unfortunately, these catalysts were only used for the decomposition of low-content N<sub>2</sub>O. When these catalysts are applied for the decomposition of high concentrations of N<sub>2</sub>O, their activities are not high enough to reduce the external energy required to initiate N<sub>2</sub>O decomposition. In recent years, some attempts have been made to find high-activity catalysts by combining noble metals with thermally stable supports. For example, mul-

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This work was supported by the National Natural Science Foundation of China (21476229, 21376236, 21503264).

DOI: 10.1016/S1872-2067(18)63077-3 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 39, No. 7, July 2018

lite and  $\text{Al}_2\text{O}_3\text{-SiO}_2$ -supported rhodium catalysts were highly active at about 350 °C [1,7]. Iridium-substituted  $\text{Al}_2\text{O}_3$  and hexa-aluminates have shown high activities and excellent thermal stabilities [8,9]. Nevertheless, in order to improve the specific activity, *i.e.* the degree of utilization of the noble metal, and to explore novel catalyst systems, further improvements of the catalytic performance are persistent pursuits.

Titania is applied in a wide range of catalysis fields, especially photocatalysis [10] and gold catalysis [11]. It is well known that titania is relatively easy to reduce and forms oxygen vacancies or other defect sites. These vacancies and defects may influence and even dictate the surface chemistry of titania, such as providing or accepting electronic charge for oxygen-related reactions [12]. In the direct decomposition of  $\text{N}_2\text{O}$ , oxygen is produced in large quantities and its desorption has been identified as the rate-determining step [13]. Hence, the facile reducibility of titania may be helpful to promote the transfer of oxygen and accelerate the decomposition of  $\text{N}_2\text{O}$  at low reaction temperatures. In addition,  $\text{IrO}_2$  has the same crystal structure as rutile  $\text{TiO}_2$ , a thermodynamically stable phase of titania's crystallographic polymorphs. The close cell parameters and comparable Ir–O and Ti–O distances were shown to be able to stabilize highly dispersed Ir species and contribute to the catalytic activity of gold particles that were deposited on top of the  $\text{IrO}_2$ , which was directly contacted with  $\text{TiO}_2$ , for CO oxidation [14]. This may also be beneficial for the decomposition of  $\text{N}_2\text{O}$ . In our previous work, a significant improvement of the catalytic activity for  $\text{N}_2\text{O}$  decomposition was observed for a  $\text{TiO}_2$ -promoted  $\text{Ir}/\text{Al}_2\text{O}_3$  catalyst [15]. With the aim of developing a more efficient catalyst and revealing its intrinsic characteristics,  $\text{TiO}_2$ -supported Ir catalysts were prepared and applied for the direct decomposition of highly concentrated  $\text{N}_2\text{O}$ .

Herein, rutile-phase titania ( $\text{r-TiO}_2$ ) was selected to prepare an Ir-supported catalyst ( $\text{Ir}/\text{r-TiO}_2$ ) using a homogeneous deposition precipitation (HDP) process. For comparison,  $\gamma\text{-Al}_2\text{O}_3$ , anatase titania, and P25-supported Ir catalysts were also prepared following the same procedures (labelled as  $\text{Ir}/\gamma\text{-Al}_2\text{O}_3$ ,  $\text{Ir}/\text{a-TiO}_2$ , and  $\text{Ir}/\text{P25}$ ). The detailed preparation processes and physical properties are included in the Supporting Information (SI). The activity evaluation was carried out in a fixed-bed flow quartz reactor. Fig. 1 shows a comparison of the catalytic activities of the different Ir catalysts (Ir loading 2 wt%) as a function of the reaction temperature. All the catalysts, though lower in Ir content when compared with those in our previous study (at least 5 wt% in general), exhibited high activities, and all were able to completely decompose  $\text{N}_2\text{O}$  below 400 °C (Table S1). This may be correlated with the high Ir utilization that resulted from the HDP preparation process that was used in this study.  $\text{Ir}/\text{r-TiO}_2$  showed the highest activity, with a light-off temperature ( $T_{50}$ ) of 265 °C (the temperature at 50%  $\text{N}_2\text{O}$  conversion), which was more than 70 °C lower when compared with the reference catalyst,  $\text{Ir}/\gamma\text{-Al}_2\text{O}_3$  ( $T_{50} = 339$  °C).  $\text{Ir}/\text{a-TiO}_2$  and  $\text{Ir}/\text{P25}$  also showed very high activities, with  $T_{50}$  values of 280 and 289 °C, respectively. These results suggest that  $\text{TiO}_2$ , particularly in the rutile form, plays an important role in the direct decomposition of  $\text{N}_2\text{O}$ . The effect of Ir loading was also evaluated. As illustrated in Fig. S1, the  $\text{N}_2\text{O}$  decomposition activity

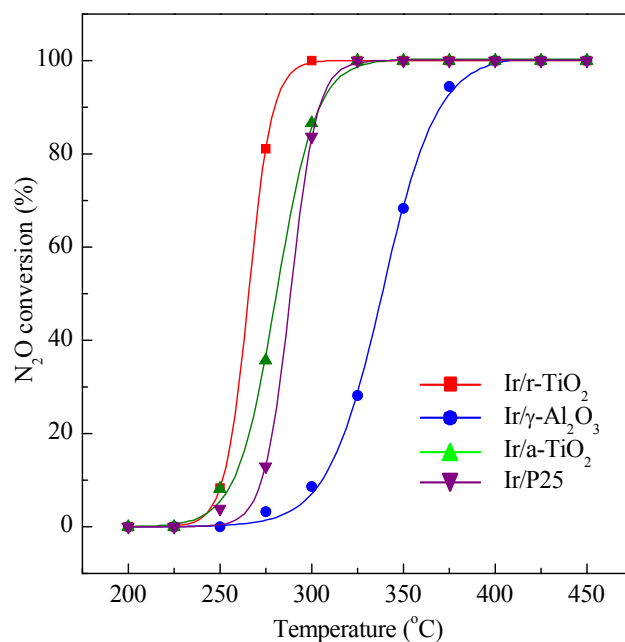


Fig. 1.  $\text{N}_2\text{O}$  conversion as a function of temperature for the Ir catalysts with different supports.

increased with higher Ir loading. When the Ir loading was 0.1%, the catalyst achieved a high activity ( $T_{50} = 338$  °C), equivalent to that of  $\text{Ir}/\gamma\text{-Al}_2\text{O}_3$ . When the Ir loading was 5%, the catalyst possessed a  $T_{50}$  of 261 °C, and exhibited the lowest temperature for 50%  $\text{N}_2\text{O}$  conversion. This trend implies that the Ir species act as the active sites in this catalytic combination. We also found that the pre-treatment with hydrogen significantly impacted the catalytic performance of  $\text{Ir}/\text{r-TiO}_2$ . As shown in Fig. S2, the  $\text{Ir}/\text{r-TiO}_2$  that was pre-reduced with  $\text{H}_2$  at 400 °C exhibited a higher catalytic activity than that without the pre-reduction. A long-term test at 300 °C was also performed with the  $\text{Ir}/\text{r-TiO}_2$  catalyst. During the 5,000-min test, the catalyst retained a high, but weakly decaying,  $\text{N}_2\text{O}$  conversion (Fig. S3).

The Brunauer-Emmett-Teller (BET) surface area of  $\text{Ir}/\text{r-TiO}_2$  (6  $\text{m}^2/\text{g}$ ) was much lower than that of  $\text{Ir}/\gamma\text{-Al}_2\text{O}_3$  (40  $\text{m}^2/\text{g}$ ), indicating that the surface area is not the primary factor for the high activity in  $\text{N}_2\text{O}$  decomposition (Table S2). The state of Ir was then measured with high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and X-ray diffraction (XRD). It can be seen, in Fig. 2(a) and (b), that the Ir species were highly dispersed on  $\text{Ir}/\text{r-TiO}_2$  with an average diameter of 1.25 nm (Fig. 2(c)). In contrast, agglomerated three-dimensional (3D) Ir nanoparticles were present on  $\text{Ir}/\gamma\text{-Al}_2\text{O}_3$  (Fig. S4). This is consistent with the XRD results (Fig. 2(d)). No diffraction peaks for the iridium species were observed for  $\text{Ir}/\text{r-TiO}_2$ , but obvious iridium diffraction peaks were observed for  $\text{Ir}/\gamma\text{-Al}_2\text{O}_3$ . The detailed Ir dispersions were also examined with pulse chemisorption of CO, as presented in Table S2, and these results further verified the above observations. Thus, the high dispersity of the Ir species on  $\text{Ir}/\text{r-TiO}_2$  is believed to be responsible for the high catalytic activity of  $\text{N}_2\text{O}$  decomposition.

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