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Communication

Superior performance of iridium supported on rutile titania for the catalytic decomposition of N₂O propellants

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ABSTRACT

N₂O 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 N₂O. In this work, we report an Ir supported on rutile TiO₂ (Ir/r-TiO₂) catalyst which exhibits a fairly high activity for high-concentration N₂O decomposition. HAADF-STEM, H₂-TPR, and XPS results indicate that highly dispersed Ir particles and improved oxygen mobility on the Ir/r-TiO₂ could facilitate the decomposition of N₂O 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 (N₂O) 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 N₂O to N₂ and O₂ 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⁻¹ [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 N₂O, *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 N₂O decomposition, completely decomposing N₂O at a temperature below 200 °C [5]. The Fe-ZSM catalyst was highly active and stable for the removal of N₂O in simulated tail-gas from nitric acid plants [6]. Unfortunately, these catalysts were only used for the decomposition of low-content N₂O. When these catalysts are applied for the decomposition of high concentrations of N₂O, their activities are not high enough to reduce the external energy required to initiate N₂O 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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lite and Al_2O_3 - SiO_2 -supported rhodium catalysts were highly active at about 350 °C [1,7]. Iridium-substituted Al_2O_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 N_2O , 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 N_2O at low reaction temperatures. In addition, IrO_2 has the same crystal structure as rutile 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 IrO_2 , which was directly contacted with TiO_2 , for CO oxidation [14]. This may also be beneficial for the decomposition of N_2O . In our previous work, a significant improvement of the catalytic activity for N_2O decomposition was observed for a 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, TiO_2 -supported Ir catalysts were prepared and applied for the direct decomposition of highly concentrated N_2O .

Herein, rutile-phase titania (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 N_2O 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% N_2O 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 TiO_2 , particularly in the rutile form, plays an important role in the direct decomposition of N_2O . The effect of Ir loading was also evaluated. As illustrated in Fig. S1, the N_2O decomposition activity

Fig. 1. N_2O 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% N_2O 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 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, N_2O conversion (Fig. S3).

The Brunauer-Emmett-Teller (BET) surface area of $\text{Ir}/\text{r-TiO}_2$ (6 m^2/g) was much lower than that of $\text{Ir}/\gamma\text{-Al}_2\text{O}_3$ (40 m^2/g), indicating that the surface area is not the primary factor for the high activity in N_2O 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 N_2O decomposition.

Fig. 2. (a, b) HAADF-STEM images of the Ir/r-TiO₂; (c) Histogram of the size distributions of Ir/r-TiO₂; (d) XRD patterns of Ir/r-TiO₂ and Ir/γ-Al₂O₃.

An H₂-TPR experiment was performed to demonstrate the redox properties of the Ir species. Fig. 3(a) shows that Ir/γ-Al₂O₃ exhibited a well-defined TPR peak at 218 °C and a weak shoulder peak at 345 °C, which can be attributed to the reduction of IrO₂ to Ir⁰ with a large particle size [16]. Whereas for Ir/r-TiO₂, two peaks centered at about 112 and 220 °C were observed. The low-temperature shift of the reduction peaks suggests that the Ir/r-TiO₂ catalyst is more easily reduced when compared with the Ir/γ-Al₂O₃ catalyst. Furthermore, Fig. 3(a) also shows that the H₂ consumption peak for Ir/r-TiO₂ in the temperature range of 50 to 400 °C was significantly larger than that for Ir/γ-Al₂O₃. This suggests that not only Ir oxides, but also Ti⁴⁺ species are partially reduced due to the typical spillover effect.

X-ray photoelectron spectroscopy (XPS) spectra were recorded to investigate the electronic state of the Ir catalysts after reduction. As illustrated in Fig. S5, Ir/γ-Al₂O₃ had a binding

energy of 60.6 eV (Ir 4f_{7/2}) after reduction at 400 °C, indicating that Ir is in a metallic state after the reduction treatment [8]. Compared to Ir/γ-Al₂O₃, the Ir 4f_{7/2} binding energy for Ir/r-TiO₂ showed a 0.3 eV shift to 60.3 eV, indicating that the Ir species in Ir/r-TiO₂ were rich in electrons. A weak Ir 4f_{7/2} peak at 61.2 eV was assigned to partially oxidized Ir^{δ+} species, which were generated from the electronic transfer between the partially reduced TiO₂ and the iridium particles [17]. The O1s XPS spectra are presented in Fig. 3(b). Ir/γ-Al₂O₃ showed a strong O1s peak centered at 531.3 eV, which can be fitted by two peaks with the binding energies of 530.9 and 531.9 eV. These were assigned to the lattice oxygen of Al₂O₃ and OH species, respectively [18]. Ir/r-TiO₂ showed two separate O 1s peaks centered at 529.7 and 532.2 eV which may be attributed to lattice oxygen O²⁻ from the metal oxides (labelled as O_α) and adsorbed oxygen belonging to a hydroxyl-like group (labelled as O_β), respectively [19]. The surface chemisorbed oxygen, O_β, has been reported to be highly active in oxygen-containing reactions due to its higher mobility over lattice oxygen [19]. Compared to the OH species of Ir/γ-Al₂O₃, the adsorbed oxygen on the Ir/r-TiO₂ surface exhibited a high binding energy transfer, indicating that these oxygen species have a higher mobility than the OH species. Therefore, the electron-rich, easy electronic transfer of the Ir species and the existence of high-mobility oxygen species on the Ir/r-TiO₂ surface could be considered as the cause which promotes the direct decomposition of N₂O.

As shown in the *in situ* N₂O-DRIFT spectra which were collected at different temperatures (Fig. 4), the adsorption of N₂O onto Ir/r-TiO₂ produced two main vibrations in the range of 2100–2400 cm⁻¹ and 1273–1302 cm⁻¹. The former bands, in the range of 2100–2400 cm⁻¹, can be attributed to the N–N stretching frequency of the N₂O that was adsorbed onto the Ir species. The latter bands, in the range of 1273–1302 cm⁻¹, are attributed to the N–O stretching modes with end-on oxygen coordinated with the metal species [M–O–NN] [20]. With increased reaction temperatures, the intensity of the two aforementioned bands decreased, suggesting that the O–N bonds of the adsorbed N₂O onto the Ir species were broken. This may be correlated with the weakening of the O–N bond that is induced

Fig. 3. (a) H₂-TPR profiles of the Ir/r-TiO₂ and Ir/γ-Al₂O₃ catalysts; (b) O 1s XPS spectra of the Ir/r-TiO₂ and Ir/γ-Al₂O₃ catalysts.

Fig. 4. *In situ* DRIFT spectra of Ir/r-TiO₂ exposed to N₂O at different temperatures following reduction.

by charge transfer involving the LUMO of N₂O and the $n+1s/nd$ orbital rehybridization at the Ir centers along with the additional interactions between the N₂O HOMO and the metal nd orbitals [21]. It should be noted that a new band at 882 cm⁻¹, attributed to the stretching mode of the bridge-bonded peroxides, appeared and increased at higher temperatures. This further indicates that peroxides are intermediate species for the N₂O decomposition [22,23].

From these findings, a plausible decomposition process of N₂O can be proposed as follows. First, nitrous oxide chemisorbs and dissociates to form gaseous nitrogen and an oxygen adatom on the surface of the iridium adjacent to the TiO₂. Second, the oxygen adatom transfers to a higher-mobility oxygen intermediate that is chemisorbed onto rutile TiO₂. Then, the nitrous oxide is further adsorbed, another oxygen adatom combines with the chemisorbed oxygen intermediate, and transforms into a diatomic O₂²⁻ ion *via* a dynamic transfer process.

Finally, the molecular oxygen desorbs from the rutile TiO₂ surface and releases an oxygen vacancy.

In conclusion, a rutile TiO₂-supported Ir catalyst was prepared *via* a HDP process and exhibited a high catalytic activity for the direct decomposition of N₂O. HAADF-STEM, H₂-TPR, and XPS measurements confirm that highly dispersed iridium is supported on the rutile titania and the improved oxygen mobility on Ir/r-TiO₂ can facilitate the decomposition of N₂O and the transfer of intermediate oxygen species. Bridge-bonded peroxide intermediates were observed through *in situ* N₂O-DRIFT, and a detailed catalytic direct decomposition mechanism of N₂O is proposed. These results will be critical for the design of new highly active catalysts and offer insight into the decomposition process of N₂O.

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Graphical Abstract

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Superior performance of iridium supported on rutile titania for the catalytic decomposition of N₂O propellants

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An Ir/r-TiO₂ catalyst exhibits high activity for the decomposition of high concentration N₂O, which is promising as a green propellant. Highly dispersed Ir particles and easy transfer of oxygen were critical for the decomposition process *via* bridge-bonded peroxide intermediates.

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金红石型氧化钛负载的铱在催化分解 N_2O 推进剂反应中的应用

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摘要: 氧化亚氮(N_2O)是一种性能独特优越的新型绿色推进剂, 分解后可以生成高温富氧燃气, 实现自增压式多种模式推进, 是小卫星推进系统理想的推进剂选择, 因而具有广阔的应用前景。在标准状态下, N_2O 热分解反应活化能为250 kJ/mol, 致使其非催化热分解温度高达600 °C, 显然小卫星的能源系统无法满足, 必须采取催化分解的手段, 改变反应路径、降低反应活化能, 使 N_2O 能够在较低的温度下分解。

有关 N_2O 分解催化剂的报道很多, 如纯相或复合氧化物、金属交换分子筛和负载贵金属等, 但是这些催化剂仍然存在活性较低等问题, 难以满足 N_2O 推进系统的应用需求。氧化钛是光催化和金催化常用的催化剂, 经还原后能够形成氧缺陷, 可以为涉氧反应提供电子, 而 N_2O 分解会产生大量氧, 氧脱附是其速率控制步骤, 因而以氧化钛为载体, 有望促进氧脱附及 N_2O 分解。与此同时, 氧化铱具有较高的 N_2O 分解活性, 而且与金红石型氧化钛晶格相似, 相似的晶格参数可能会促进其在氧化钛表面的分散, 进一步提高 N_2O 分解性能。基于此, 本文以金红石氧化钛(r-TiO_2)为载体, 采用匀相沉积沉淀法制备了不同载量的金红石氧化钛负载铱催化剂(Ir/r-TiO_2), 并制备了锐钛矿型氧化钛、混合晶相P25和 $\gamma\text{-Al}_2\text{O}_3$ 负载铱催化剂作为对比。

通过活性测试我们发现, Ir/r-TiO_2 催化剂显示了非常优异的 N_2O 分解活性, N_2O 转化率明显高于参比催化剂, 在250 °C就能够开始分解, 在300 °C可以分解完全, 而且当Ir含量降低到0.1 %时, 催化剂仍然保持与2 wt% $\text{Ir}/\gamma\text{-Al}_2\text{O}_3$ 相当的催化活性。

随后我们采取多种表征手段对 Ir/r-TiO_2 的活性本质和 N_2O 分解机理进行了探究。首先利用BET、HAADF-STEM和XRD对催化剂的基本物性进行了测试, 发现 Ir/r-TiO_2 具有较低的比表面积, 但金属铱在金红石氧化钛表面表现出较高的分散度, 平均粒径仅为1.25 nm。采用 H_2 -TPR和O 1s XPS考察了催化剂的电子特性和还原特性, 发现 Ir/r-TiO_2 催化剂上高分散的Ir与氧的结合能较弱, 易于还原, 有助于 N_2O 的分解和生成氧的脱附。进一步采用原位 N_2O -DRIFT对 N_2O 分解过程进行了研究, 发现了桥式过氧物种, 并据此提出了 N_2O 在 Ir/r-TiO_2 催化剂上的分解机理。

关键词: 多相催化; 氧化亚氮; 催化分解; 铱催化剂; 二氧化钛

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