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Superior performance of Ir-substituted hexaaluminate catalysts for N_2O decomposition

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Abstract

Novel Ir-substituted hexaaluminate catalysts were developed for the first time and used for catalytic decomposition of high concentration of N_2O. The catalysts were prepared by one-pot precipitation and characterized by X-ray diffraction (XRD), N_2-adsorption, scanning electronic microscopy (SEM) and temperature-programmed reduction (H_2-TPR). The XRD results showed that only a limited amount of iridium was incorporated into the hexaaluminate lattice by substituting Al^{3+} to form $BaIr_xFe_{1-x}Al_{11}O_{19}$ after being calcined at 1200 °C, while the other part of iridium existed as IrO_2 phase. The activity tests for high concentration (30%, v/v) of N_2O decomposition demonstrated that the $BaIr_xFe_{1-x}Al_{11}O_{19}$ hexaaluminates exhibited much higher activities and stabilities than the Ir/Al_2O_3-1200, and the pre-reduction with H_2 was essential for activating the catalysts. By comparing $BaIr_xFe_{1-x}Al_{11}O_{19}$ with $BaIr_xAl_{12-x}O_{19}$ ($x = 0$–0.8), it was found that iridium was the active component in the N_2O decomposition and the framework iridium was more active than the large IrO_2 particles. On the other hand, Fe facilitated the formation of hexaaluminate as well as the incorporation of iridium into the framework.

Keywords: N_2O decomposition; Iridium; Hexaaluminate; Propellant

1. Introduction

The catalytic decomposition of nitrous oxide (N_2O) has received growing interest because of its environmental effect [1]. Most of studies are focused on catalytic decomposition of low concentration of N_2O. Various catalytic systems have been found to be effective for N_2O decomposition, such as supported noble metals [2,3], spinels [4,5], ex-hydrotalcites [6–9] and zeolites [10–12].

However, from another point of view, N_2O is being regarded as a promising green propellant for space propulsion due to its extremely low toxicity compared to traditional hydrazine propellant [13–15]. For this special application, activity is not the only parameter to be considered. Due to the highly exothermic nature of this reaction (the adiabatic decomposition temperature can reach ~1640 °C), the high-temperature stability of catalytic materials is the main challenge for the application of N_2O as a propellant. It has been reported [16] that Ir/Al_2O_3 (Shell 405) had a high activity towards the decomposition of N_2O. However, upon being subjected to the high-temperature treatment (1200 °C), the active components Ir or IrO_2 showed signs of sintering and the alumina support began to irreversibly convert to α-Al_2O_3, thereby drastically reducing the surface area and leading to the activity loss. Therefore, with respect to the thermal stability, many previous catalyst systems used for low concentration N_2O decomposition will not be suitable for high concentration N_2O decomposition, either for the collapse of catalyst structure or the sublimation of active component at high temperatures. A preliminary test on Ni-Co-Zr-O catalyst [16] demonstrated that such a mixed oxide was thermally stable even at 1200 °C, but less active than the shell 405.

Recently, the need for catalysts that remain stable and active over long periods at high operation temperatures—such as energy generation through natural gas combustion, steam reforming and the partial oxidation of hydrocarbons, prompts the rapid development of highly thermal stable catalytic materials. For example, various heat-resistant metal oxides have been tested as catalysts or catalyst supports for the combustion of methane, such as hexaaluminate [17–19],

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perovskites [20], or even SiC [21]. Among them, hexaaluminates [22] are considered to be one of the most promising catalysts for this reaction due to their excellent thermal stability and high activity. Moreover, the hexaaluminates can contain catalytically active components in their structures [20,23], thereby inhibiting loss of active component at high temperatures before the structural collapse. In spite of these obvious advantages, most studies on the hexaaluminates so far have been for methane combustion [24–27], whereas their applications to catalytic decomposition of N_2O under severe conditions have been scarcely investigated. In a very recent report, a $BaFeAl_{11}O_{19}$ hexaaluminate catalyst was applied for N_2O abatement in industry but it only showed poor activity [28]. By contrast, we reported Ir-substituted hexaaluminates in our previous communication [29], and found that they were highly active and stable catalysts for N_2O decomposition. In the present work, we made a detailed study on this Ir-substituted hexaaluminates system, with focus on the role played by the framework Ir and Fe in the N_2O decomposition.

2. Experimental

2.1. Catalyst preparation

Ba-Ir-Fe-Al oxide catalysts ($BaIr_xFe_{1-x}Al_{11}O_{19}$, denoted as BIFA-t, t indicates calcination temperature) were prepared by one-pot precipitation [24]. Typically, to prepare $BaIr_{0.2}Fe_{0.8}Al_{11}O_{19}$ ($x = 0.2$), 0.95 g $Ba(NO_3)_2$, 0.90 g 44 wt% H_2IrCl_6, 15.03 g $Al(NO_3)_3{\cdot}9H_2O$ and 1.16 g $Fe(NO_3)_3{\cdot}9H_2O$ were dissolved individually in deionized water at 60 °C, and then mixed together with the pH adjustment with dilute HNO_3 solution to ∼1. The resulting mixture solution was then poured with vigorous stirring into a saturated $(NH_4)_2CO_3$ aqueous solution at 60 °C to form the hexaaluminate precursor precipitate. During the precipitation, a large amount of CO_2 was released while the pH value of the solution was maintained between 7.5 and 8.0. The precipitate was aged with continuous stirring in the mother liquor at 60 °C for 3 h followed by filtration and washing with deionized water. The recovered solid was then dried at 120 °C overnight and calcined at 500 °C in air for 2 h. In some cases, further calcinations were conducted at 800, 1000, 1200 or 1400 °C for 4 h in air. For comparison, Ba-Fe-Al (denoted as BFA) and Ba-Ir-Al (denoted as BIA) oxide catalysts were prepared with the same procedure as that for BIFA, without the addition of H_2IrCl_6 or $Fe(NO_3)_3{\cdot}9H_2O$. On the other hand, Ir/Al_2O_3 was prepared by the above precipitation procedure with $Al(NO_3)_3{\cdot}9H_2O$ and H_2IrCl_6 as the starting materials.

2.2. Catalytic activity measurements

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 quartz reactor. Prior to the reaction, the catalyst sample was pre-reduced with pure H_2 at 400 °C 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 50 ml/min, corresponding to a gas hour space velocity (GHSV) of 30,000 ml/h g. The catalyst temperature was measured using a thermocouple situated close to the catalyst sample. The effluent gas was on-line analyzed by Agilent 6890N gas chromatograph equipped with Chromosorb 103 column and Porapak Q columns. N_2O conversion based on the difference between the inlet and outlet concentration was used as evaluation of the catalytic activity.

2.3. Characterization

The BET specific surface areas were measured by nitrogen adsorption at −196 °C on a Micromeritics ASAP 2010 apparatus. The samples were evacuated firstly at 110 °C for 3 h and then at 350 °C for 5 h prior to their analysis.

Powder X-ray diffraction (XRD) patterns were obtained with a D/Max-βb diffractometer using a Cu Kα radiation source ($\lambda = 0.15432$ nm). The spectra were scanned between $2\theta = 10–80°$. Unit cell parameters were calculated by the least squares method.

Scanning electron microscopy (SEM) experiments were performed with a JSM 6360-LV electron microscope operating at 20–25 kV. The samples were vapor-deposited with gold before analysis.

The actual Ir loadings of the catalysts were determined by Thermo IRIS Interepid II inductively coupled plasma (ICP) after having dissolved solid in a mixture of concentrated acids (HF + HCl + HNO_3).

Temperature-programmed reduction of H_2 (H_2-TPR) was performed on a Micromeritics Autochem 2920 apparatus. A 100-mg sample was used for each measurement. The samples were pre-treated in a flow of Ar at 200 °C for 1 h with a heating rate of 10 °C/min. After cooling to 40 °C in Ar, the feed gas was switched to 10% H_2–Ar mixture. Then, temperature was raised from 40 to 900 °C at a rate of 10 °C/min. A thermal conductivity detector (TCD) was used on line for measuring H_2 consumption.

3. Results and discussion

3.1. Evolution of hexaaluminate BIFA

It has been reported [30–32] that the hexaaluminate Ba-Fe-Al oxide could be formed by calcining the corresponding precursor at above 1100 °C. In the present work, we tried to incorporate precious metal Ir into the Ba-Fe-Al oxide mixture. The phase transformation of the Ba-Ir-Fe-Al oxide during the calcination process was monitored by XRD technique. Fig. 1a shows the XRD patterns of the Ba-Ir-Fe-Al oxide with an increase in the calcination temperature. For comparison, the XRD patterns of the Ir/Al_2O_3 calcined at different temperatures are also shown in Fig. 1b. It can be seen that calcining the Ba-Ir-Fe-Al oxide precursor at 500 °C yielded only IrO_2 and γ-Al_2O_3 crystalline phases, no other metal oxides could be detected with XRD, indicating amorphous nature or a highly dispersed state of Ba-Fe oxides on the Al_2O_3 support [23]. The presence of