Catalysis Today xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Plasma-catalytic decomposition of nitrous oxide over γ-alumina-supported metal oxides

Jin-Oh Jo[a], Quang Hung Trinh[a], Seong H. Kim[b], Young Sun Mok[a,b,*]

[a] Department of Chemical and Biological Engineering, Jeju National University, Jeju 690-756, Korea
[b] Department of Chemical Engineering, Pennsylvania State University,University Park, PA 16802, USA

ARTICLE INFO

Keywords:
Plasma-catalytic
Nitrous oxide
Decomposition
Metal oxides

ABSTRACT

This work investigated the decomposition of dilute N_2O from gas streams with various oxygen contents by using a plasma-catalytic process over metal oxide catalysts supported on γ-Al_2O_3. Among the metals explored (Ru, Co, Cu, V, etc.), Ru was found to be the best catalyst for the decomposition of N_2O in a plasma-catalytic reactor, and most of the experiments were conducted with alumina-supported Ru. The effects of applied voltage, reaction temperature, O_2 content, gas flow rate and initial N_2O content on the decomposition efficiency and byproducts formation were examined. Compared to the catalyst-alone case, the presence of plasma enhanced the decomposition efficiency by 30–50%, depending on the operating condition. The increase in the oxygen content from 0 to 20% largely decreased the catalytic decomposition efficiency, whereas in the presence of plasma N_2O could be successfully decomposed even at 20% O_2 content. The decomposition efficiency was not a strong function of the initial N_2O concentration in the range of 225–1800 ppm, exhibiting pseudo first-order reaction kinetics. Without O_2, there were negligible byproducts, but in the presence of O_2, NO and NO_2 were formed mainly due to the plasma-induced reactions between background molecules such as N_2 and O_2. The results obtained in this work showed the feasibility of plasma-catalytic process for the abatement of N_2O.

1. Introduction

Nitrous oxide (N_2O) emitted from various human activities including agriculture, industrial processes, fossil fuel combustion and wastewater management is one of the major non-CO_2 greenhouse gases. It is estimated to have a global warming potential (GWP) ~300 times that of CO_2 for a 100-year time horizon [1]. The technological options to reduce N_2O emissions are generally based on catalysis, even though thermal destruction techniques are also available in cases that N_2O is highly concentrated (e.g., adipic acid plants). When the concentration of N_2O is low in the off-gas stream as in a nitric acid plant, non-selective catalytic reduction (NSCR) can be a measure. While NSCR is known to be effective in reducing N_2O emissions by ~90%, additional fuel is required for this process, increasing the operation cost [2]. At present, it appears that there is no commercially available technology developed to reduce N_2O emissions from stationary and mobile combustions, indicating that more research is needed to develop cost-effective and reliable technologies.

Recently, it has been reported that catalytic processes coupled with non-thermal plasma can be promising in treating a variety of air contaminants such as volatile organic compounds (VOCs), nitrogen oxides (NO_x) and halogenated hydrocarbons [3–7]. The same principles of plasma-catalysis that works for the treatment of VOCs, NO_x and halocarbons can also apply in the decomposition of N_2O, but it has been relatively less investigated [8,9]. Schmidt-Szałowski et al. [8] applied the gliding arc plasma combined with a catalytic bed to N_2O processing. They found that in the presence of oxygen N_2O is either oxidized to NO or decomposed to O_2 and N_2 by gliding arc plasma and several alumina-supported metal oxide catalysts (CuO, Fe_2O_3, etc.) combined with plasma catalyze N_2O conversion into O_2 and N_2. Lee and Kim [9] investigated the argon plasma coupled with Ru/alumina catalyst for the decomposition of N_2O, and they reported that argon plasma could break the chemically stable N_2O bonds to form NO, N and O radicals even at low temperatures and the plasma-generating species could be more reactive on the active sites of the catalyst than in the gas phase. Since their experiments were performed under no-oxygen condition, however, it was not explained how oxygen plays a role in the N_2O decomposition. Moreover, the results obtained with N_2O-Ar mixture may not be realistic because the emissions of N_2O in real situations are not likely in argon atmosphere. Meanwhile, in traditional thermal catalysis, the catalytic activity largely depends on the type of metal oxide catalyst. According to Taniou [10], Ru, Pd and Rh oxides are

* Corresponding author at: Department of Chemical and Biological Engineering, Jeju National University, Jeju 690-756, Korea.
E-mail address: smokie@cheju.ac.kr (Y.S. Mok).

http://dx.doi.org/10.1016/j.cattod.2017.05.028
Received 10 January 2017; Received in revised form 29 March 2017; Accepted 5 May 2017

highly active for the N_2O decomposition, while Fe, Ni, Cu and In oxides exhibit relatively poor activities. Likewise, the plasma-catalytic activity for the N_2O decomposition can also be affected by the type of catalyst, which needs to be examined under the influence of plasma. As well, when a catalyst is used, the N_2O decomposition efficiency can be very sensitive to O_2 content [11,12].

In this work, the plasma-catalytic decomposition of N_2O was investigated over γ-alumina-supported metal oxide catalysts, giving the first consideration to RuO_2/γ-alumina through a screening test. A one-stage plasma-catalytic reactor in which the catalyst pellets were in direct contact with alternating-current (AC) driven plasma was employed for this work. The inhibitory effect of the oxygen content in N_2-O_2-N_2O mixture on the N_2O decomposition was examined in the range up to 20% by volume. The process variables evaluated in this work included applied voltage, feed gas flow rate, inlet N_2O concentration and reaction temperature.

2. Experimental section

2.1. Catalyst preparation

The supported catalysts were prepared by impregnating γ-Al_2O_3 pellets with aqueous solutions of metal precursors. As an example, for the preparation of Ru/γ-Al_2O_3, a given amount of γ-Al_2O_3 pellets (length: 3.2–3.5 mm; diameter: 3.2 mm; Alfa Aesar, USA) was impregnated with an aqueous solution of $RuCl_3$ (Sigma-Aldrich, USA). The Brunauer-Emmett- Teller (BET) specific surface area of the γ-Al_2O_3 pellets was measured to be 216.5 $m^2\ g^{-1}$ by a surface area and pore size analyzer (Autosorb-1-mp, USA). After the impregnation, drying overnight at 110 °C and calcining at 550 °C for 6 h in air atmosphere were performed. A series of other supported catalysts (Ag/γ-Al_2O_3, Ce/γ-Al_2O_3, Co/γ-Al_2O_3, Cu/γ-Al_2O_3, Fe/γ-Al_2O_3, Ni/γ-Al_2O_3, V/γ-Al_2O_3) were also prepared in the same way by impregnating the γ-Al_2O_3 pellets with the aqueous solutions of $AgNO_3$ (99.8%, Daejung, Korea), $Ce(NO_3)_3{\cdot}6H_2O$ (99%, Yakuri Pure Chemicals Co., Japan), $CoN_2O_6{\cdot}6H_2O$ (98%, Sigma-Aldrich), $Cu(NO_3)_2{\cdot}3H_2O$ (99%, Daejung, Korea), $Fe(NO_3)_3{\cdot}6H_2O$ (99%, Daejung, Korea), $NiN_2O_6{\cdot}6H_2O$ (99%, Daejung, Korea) and NH_4VO_3 (99%, Junsei, Japan). When calcination is carried out at 550 °C for 6 h under the air atmosphere after the impregnation and drying, nitrate, ammonium and chlorine are all thermally decomposed and released [10,13,14]. The metal loading in the prepared catalysts was 2.0 wt%.

2.2. Experimental methods

Fig. 1 shows the schematic of the present plasma-catalytic reactor comprising an alumina ceramic tube (inner diameter: 26 mm; thickness: 2 mm), catalyst pellets (26 g or 35 mL), a concentric threaded stainless steel rod (diameter: 6 mm) acting as the discharging electrode, and a ground electrode (aluminum foil; length: 80 mm) wrapping around the ceramic tube. The plasma-catalytic reactor was energized by an AC high voltage (400 Hz) in the range of 12–26 kV (peak value). As understood from Fig. 1, plasma was generated in the catalyst-packed bed, so that the plasma was in direct contact with the catalyst pellets. The feed gas was prepared by mixing O_2, N_2 and N_2O whose flow rates were controlled using mass flow controllers (AFC 500, Atovac, Korea). The typical O_2 and N_2O contents in the feed gas were 10% by volume and 450 ppm (parts per million, volumetric). The effect of the oxygen content was examined in the range up to 20%, while that of the N_2O concentration in the range of 225–1800 ppm. The flow rate of the feed gas was typically 1.0 L min^{-1}, and varied from 0.5 to 2.0 L min^{-1}. So as to investigate the effect of reaction temperature on the N_2O decomposition, the plasma-catalytic reactor was installed in a temperature-controlled tube furnace. The reaction temperature was changed from 200 to 350 °C. Plasma discharge in N_2-O_2 mixture can generate NO and NO_2. The catalyst bed (Ag/γ-Al_2O_3) right after the plasma-catalytic reactor is for the reduction of NO_x (NO and NO_2). The amount of the Ag/γ-Al_2O_3 catalyst for NO_x reduction was 7.5 g.

The N_2O concentration was analyzed by a Fourier transform infrared spectrophotometer (FTIR-7600, Lambda Scientific, Australia) equipped with a 16 cm long homemade gas cell. For the FTIR measurements, the resolution was set to 1.0 cm^{-1}, and ten IR spectra were taken at a given experimental condition to take an average. The concentrations of NO_x (NO and NO_2) formed as byproducts were measured by a NO_x analyzer (rbr-ecom KD, rbr-Computertechnik GmbH, Germany). The applied voltage across the plasma-catalytic reactor was measured with a digital oscilloscope (DPO3034, Tektronix, USA) and a 1000:1 high voltage probe (P6015, Tektronix, USA). The discharge power was determined by the so-called Lissajous charge-voltage figure [15]. The discharge power values at different reaction temperatures are presented as a function of applied voltage in Fig. 2.

3. Results and discussion

3.1. Plasma-catalytic activities of metal oxides

The effect of several γ-alumina-supported metal oxide catalysts on the plasma-catalytic decomposition of N_2O is shown in Fig. 3. The decomposition was carried out in the presence of 10% O_2 at applied voltages in the range of 13.2–25.6 kV. When high voltage was not applied, i.e., at 0 kV, the catalyst separately exerted action on the decomposition of N_2O. Generally, the N_2O decomposition efficiency increased with increasing the voltage for all the catalysts. This is because more reactive species were generated at a higher voltage. When plasma is created, a variety of reactive species are formed by processes such as excitation, ionization and dissociation, including excited N_2 molecules, N radicals and N_2 ions. These species decompose N_2O as follows (see Refs. [16–19] for reactions (1)–(4) respectively):

$$N_2(A^3\Sigma_u^+) + N_2O \rightarrow 2N_2 + O,\ k_1 = 3.97 \times 10^{12} cm^3 mol^{-1} s^{-1} \quad (1)$$

$$N_2(a'^1\Sigma_u^-) + N_2O \rightarrow \text{products},\ k_2 = \times 10^{14} cm^3 mol^{-1} s^{-1} \quad (2)$$

$$N(^2D) + N_2O \rightarrow N_2 + NO,\ k_3 = 1.32 \times 10^{12} cm^3 mol^{-1} s^{-1} \quad (3)$$

$$N_2^+ + N_2O \rightarrow N_2 + N_2O^+,\ k_4 = 3.61 \times 10^{14} cm^3 mol^{-1} s^{-1} \quad (4)$$

where the rate constants in reactions (1)–(4) are at 298 K. The N_2O decomposition efficiency largely depended on the type of catalyst used. As seen, Ru, Cu and Ce supported on γ-alumina exhibited catalytic activity for the N_2O decomposition, among which the decomposition efficiency with Ru/γ-alumina was the highest. At a voltage of 25.6 kV, the N_2O decomposition efficiency with Ru/γ-alumina was enhanced by approximately 40% in comparison with the bare γ-alumina case. On the other hand, Ag, Co, Fe, Ni and V oxides supported on γ-alumina showed no or negative catalytic activity under plasma discharge condition, probably due to reversible adsorption and desorption of O_2 onto the active sites [12]. According to the literature [20], Ru in a valence state more than 4 exhibits a tendency for tetrahedral coordination, and thus, Ru surface atoms, with a valence state ≥ 4 and tetrahedrally coordinated, can interact with N2O, changing their coordination. On Ru sites with high reactivity and unsaturated coordination, the following reaction can occur:

$$RuO_2 + N_2O \rightarrow RuO_3 + N_2 \quad (5)$$

RuO_3 and RuO_2 are in equilibrium:

$$2RuO_3 = 2RuO_2 + O_2 \quad (6)$$

Further reaction to decompose N_2O can occur by RuO_3 as follows:

$$RuO_3 + N_2O \rightarrow RuO_2 + N_2 + O_2 \quad (7)$$

This reaction evolves oxygen, thereby regenerating the active sites. In