



Removal of dilute nitrous oxide from gas streams using a cyclic zeolite adsorption–plasma decomposition process

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HIGHLIGHTS

- Ca13X was effective for dilute N₂O adsorption.
- Ca13X packed-bed DBD reactor was developed for cyclic removal of dilute N₂O.
- Cyclic operation was more energy-efficient than continuous operation.
- Plasma-induced heat desorbed the adsorbed N₂O, which was decomposed in gas phase.

ARTICLE INFO

Article history:

Received 11 March 2016

Received in revised form 5 May 2016

Accepted 6 May 2016

Available online 7 May 2016

Keywords:

Nitrous oxide
Nonthermal plasma
Adsorption
Decomposition
Zeolite
Ion exchange

ABSTRACT

Removal of dilute N₂O from gas streams by a cyclic adsorption–decomposition using Ca13X (Ca²⁺ exchanged 13X) in combination with N₂ nonthermal plasma was studied in this work. Zeolite 13X was found to be the best for N₂O uptake among tested commercial zeolites including 4A, H-β and 13X. By modifying 13X with Ca²⁺ cation using ion-exchange method, the N₂O adsorption capacity was greatly enhanced from *ca.* 3.5×10^{-6} to 80×10^{-6} mol g_{zeolite}⁻¹ due to the stronger interaction of N₂O with Ca²⁺ cation than that with Na⁺ cation. *Ca.* 96% of N₂O removal efficiency at a *SIE*_{eq} (equivalent specific input energy) of 1116 J L⁻¹ was obtained under the cyclic operation of 60-min N₂O adsorption (initial concentration: 510 ppm, gas flow rate: 0.5 L min⁻¹) over Ca13X followed by 20-min plasma decomposition of adsorbed N₂O in stationary N₂ atmosphere. In comparison, a similar performance was reached at a relatively high *SIE* of 1700 J L⁻¹ as the reactor was operated under continuous plasma condition. The time period of plasma step and therefore the energy consumption could be reduced by properly circulating N₂ gas in the reactor. Also, *SIE*_{eq} was found to decrease with increasing the adsorption time, whereby *ca.* 95% of N₂O removal efficiency could be achieved at a *SIE*_{eq} of 298 J L⁻¹ as the adsorption time was 180 min. The regeneration of N₂O-adsorbed Ca13X by N₂ plasma was initiated by plasma-induced desorption of adsorbed N₂O followed by decomposing the desorbed N₂O in plasma gas phase.

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1. Introduction

Nitrous oxide (N₂O) is a strong greenhouse gas, which has a large global warming potential of 310 and contributes *ca.* 6% to global warming. In addition, as migrating to the stratosphere, N₂O reacts with ozone, causing the destruction of the ozone layer and formation of stratospheric NO_x [1–3]. The N₂O atmospheric concentration has been increasing at an annual growth rate of 0.2–0.3% since the middle of the 20th century due to anthropogenic practices such as agriculture (soil cultivation and the use of

nitrogen-fertilizers), chemical processes (production of adipic and nitric acids), energy industry (burning of organic material and fossil fuels) and transportation (a side-effect of the introduction of the catalytic converter to control NO_x) [4].

The increasingly adverse effects of N₂O on the environment have raised a considerable attention to many researchers to develop effective methods for N₂O abatement [5–8] including thermal decomposition, selective catalytic reduction and catalytic decomposition [1]. Both noble and non-noble metal based catalysts have been investigated to show high removal efficiency; however, the operating temperature is still high, usually above 300 °C [9–11]. In an effort to find out an alternative method, non-thermal plasma (NTP) which can be stably generated under normal atmospheric conditions were recently tested for direct

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decomposition of N₂O in nitrogen and argon plasmas [12–14]. For nitrogen plasma, the conversion of N₂O was proposed to occur through interaction of N₂O with plasma-induced active nitrogen species such as N(²D), N₂(A³Σ_u⁺) and N₂⁺ [15]. Meanwhile, in argon plasma, it was explained by electron impact and collision with electronic excited Ar, Ar(³P₂) [13,16]. The direct removal of N₂O from air by NTP is probably not effective due to the intrinsic formation of nitrogen oxides (NO, NO₂ and N₂O) in air plasma [17,18]. Therefore, from practical point of view, using adsorption to remove N₂O from exhausted oxygen-containing gases before decomposing the adsorbed N₂O by N₂ plasma could be a feasible way for N₂O abatement. In such a cyclic process, a long-time adsorption step followed by a short-time decomposition one leads to a reduction of energy consumption.

In this work, screening commercial zeolites including 4A, H-β and 13X for adsorption of dilute N₂O in air under flowing condition at room temperature was performed. Chosen zeolite adsorbent was modified by ion-exchanged method in order to improve the adsorption capacity and then was combined with N₂ plasma for N₂O abatement. To the extent of our knowledge, this is the first work that investigated the direct regeneration of N₂O-adsorbed zeolite by N₂ plasma in a dielectric barrier discharge (DBD) plasma reactor. The effects of plasma-on time, amount of N₂O adsorbed on the reactor performance were evaluated. In addition, the use of gas circulation during plasma decomposition step was tested for optimizing the plasma-on time and reducing energy consumption. The energy consumed in terms of specific input energy (*i.e.*, energy per unit volume of treated gas) was then compared with that of the conventional continuous treatment (*i.e.*, plasma continuously ignited for N₂O abatement without adsorption). Also, the mechanisms for N₂O decomposition and adsorbent regeneration were elucidated by investigating N₂O conversion on different packing materials with and without co-existing gases (H₂O, CO and CO₂), N₂O thermal desorption as well as plasma-induced reactor temperature.

2. Experimental

2.1. Experimental setup

Fig. 1(a) depicts the experimental setup consisting of a cylindrical DBD reactor energized by an AC power source at a repetition rate of 400 Hz. The DBD reactor was composed of a high voltage (HV) electrode (stainless steel, diameter: 5.5 mm) placed coaxially inside a quartz tube (inner diameter: 25.5 mm, thickness: 2 mm, length: 550 mm) acting as the dielectric. The ground electrode made of aluminum foil was wrapped outside the quartz tube, resulting in a discharge region of 112 mm long. Depending on specific experiment, this active region was either left blank or fully filled with pelleted adsorbents (weight: 30 g). The system was designed in a way that plasma steps could be performed under stationary (*i.e.*, the reactor was closed) and/or flowing conditions by gas circulation (*i.e.*, circulating condition). When gas circulation was performed, the external N₂ gas supplied from a cylinder was switched off, and the reactor was connected to a circulating pump whose pumping flow rate was adjusted at 0.5 L min⁻¹ by a flowmeter. Circulation direction was changeable by changing the order connection of the reactor with the pump inlet and outlet. All adsorption steps were carried out under forward flow condition where the simulated gas flowed through the reactor from left to right of Fig. 1(a). It is noted that plasma ignition was performed in N₂ atmosphere for all cases therefore the reactor, pump and gas lines were flushed with nitrogen gas before connection and plasma initiation. The N₂O plasma decomposition could be also conducted under continuous operation. In this mode, N₂O diluted in N₂ gas was continuously fed to the reactor and plasma was

simultaneously turned on at a desired applied voltage. The remaining N₂O in the reactor after plasma decomposition was evaluated via thermal desorption. Before this step, the reactor was cooled down to room temperature and was simultaneously circulated to re-adsorb the desorbed N₂O existing in the dead space of the reactor, if any. During the thermal desorption, the reactor was placed inside an electrical furnace whose temperature was set to increase from 25 to 300 °C at a ramping rate of 10 °C min⁻¹. Also, during this step, the reactor was continuously fed with pure N₂ gas (flow rate: 0.5 L min⁻¹) in the forward direction, otherwise mentioned.

2.2. Materials and methods

The N₂O contaminated gas was made by diluting N₂O with either synthetic air or N₂ gas at a N₂O concentration of 510 ppm. Gas composition and flow rate were controlled by mass flow controllers (MFC). All N₂O adsorption tests were performed under atmospheric conditions without plasma ignition. CO, CO₂ and water vapor were individually added to N₂O contaminated gas flow to investigate their influence on N₂O adsorption and decomposition. The relative humidity (RH) was controlled by using a CO₂ and RH monitor (ZG106R, ZyAura). Gaseous samples from the reactor outlet were identified and quantified by a Fourier-transform infrared (FTIR) spectrometer (FTIR-7600, Lambda Scientific) equipped with a 160-mm-long gas cell. The N₂O removal efficiency for cyclic operation is estimated as follows:

$$\eta_{\text{cyclic}} (\%) = \frac{F_{\text{ads}} \int_0^{T_{\text{ads}}} (C_{\text{initial}} - C_{\text{ads}}) dt - F_{\text{des}} \int_0^{T_{\text{des}}} C_{\text{des}} dt}{F_{\text{ads}} \cdot C_{\text{initial}} \cdot T_{\text{ads}}} \times 100 \quad (1)$$

where F_{ads} (or T_{ads}) and F_{des} (or T_{des}) are the gas flow rates (or time periods) of the adsorption and thermal desorption steps in L min⁻¹ (or min), respectively. C_{initial} is the initial N₂O concentration, and C_{ads} and C_{des} are outlet N₂O concentrations during the adsorption and thermal desorption steps in ppm, respectively. Meanwhile, the removal efficiency for continuous operation at the steady state is calculated by:

$$\eta_{\text{continuous}} (\%) = \frac{C_{\text{initial}} - C_{\text{out}}}{C_{\text{initial}}} \times 100 \quad (2)$$

where C_{out} is the outlet N₂O concentration in ppm at the steady state.

In order to monitor the actual reactor temperature during N₂O thermal desorption, a thermocouple was inserted into the zeolite packed region. Meanwhile, to examine the heating effect induced by plasma discharge on N₂O desorption, the infrared (IR) images of reactor were taken in a dark room using a thermal imager (Fluke, Ti32). The measurement setup is shown in Fig. 1(b), in which the reactor whose upper side opening was kept vertically aligned with the thermal imager. Before taking images, 0.5 L min⁻¹ N₂ gas was delivered to the reactor from the lower side, while the applied voltage was fixed at a desired value for a specific period of time.

Three different commercial zeolites including 4A, H-β and 13X (average diameter: 4 mm, weight: 30 g for each, Cosmo Fine Chemicals) were chosen as the adsorbents for N₂O adsorption tests. Zeolite 13X was modified with Ca²⁺ cation using ion-exchanged method. In this method, 70 g of the pelleted 13X was soaked in 0.6 L of 0.2 M aqueous solution of Ca(NO₃)₂ (Dae Jung, Korea) for 3 h under stirring condition at 80 °C. The process was repeated 2 times before softly rinsing the zeolite with distilled water. The Ca²⁺ exchanged 13X denoted as Ca13X was dried overnight in a dry oven and subsequently calcined at 500 °C for 3 h in ambient air using an electrical furnace. The Brunauer–Emmett–Teller (BET) surface areas of the parent 13X and Ca13X were measured using a surface area analyzer (TriStar II 3020, Micromeritics) to be 726 and 370 m² g⁻¹, respectively.

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