Investigation on Catalytic N$_2$O Conversion to NO for Potential Nitric Acid Production from Industrial Waste Gas

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Abstract. It is well known that N$_2$O has a very significant impact on the greenhouse effect. Although N$_2$O is not the major contributor to the global warming, while it could stay in atmosphere for about 150 years, and its global warming potential (GWP) is about 2.5 and 310 times as that of CH$_4$ and CO$_2$, respectively. The main source of N$_2$O emission from chemical industries is originated from the process of adipic/nitric acid production. The emission of N$_2$O due to adipic acid production in China is about 0.48–0.72 million tons per year based on the mass ratio between N$_2$O emission and adipic acid production, which is equivalent to 150–250 million tons CO$_2$ emission. However, there are few reports on economically reusing N$_2$O from flue gas by direct oxidation method. Therefore, a series of catalysts applied on catalytic N$_2$O conversion to NO for potential production of nitric acid from flue gas have been prepared by co-precipitation method. The basic property of catalysts was characterized by BET, laser particle size analyzer, FT-IR, TG/DTA, and CO$_2$-TPD, etc. The catalyst’s performance was evaluated in a fixed-bed reactor with mixture of 40%(v)N$_2$O+40%(v)N$_2$+20%(v)O$_2$ under 3000h$^{-1}$ space velocity and 0.1MPa system pressure. Results showed that catalysts of Pt/Cu-ZnO and Pt/Zr-Zn-O have good selectivity on NO production, which was about 10% and 15%, respectively, in the temperature range from 550°C to 650°C. The basic experimental results show that it is a promising method to be applied for N$_2$O reuse in adipic acid production and nitric acid industries and also provide the basis for further relative theoretical and experimental studies.

1. Introduction

N$_2$O is the main component of NOx in stratosphere. N$_2$O has a very significant impact on the greenhouse effect, which is due to its strong absorption of infrared radiation. Although N$_2$O is not a major contributor to the global warming, its influence is much greater than CO$_2$ and CH$_4$ as it could last in atmosphere for about 150 years [1-5], and its global warming potential (GWP) is about 2.5 and 310 times as that of CH$_4$ and CO$_2$, respectively. Generally, the biological process occurring in the soil and ocean is the main source of N$_2$O, while the use of nitrogen fertilizer contributes about 57% of total N$_2$O emission. Meanwhile, chemical production, combustion of fossil and organic fuel is also the main source, in which the process of adipic acid production and nitric acid used is the main source of N$_2$O emission [6-12]. Normally, the mass ratio between N$_2$O emission and adipic acid production would be between 0.24–0.36, thus, the emission of N$_2$O due to adipic acid production in China is about 0.48–0.72 million tons per year, which is equivalent to 150–250 million tons CO$_2$ emission [13-17].

However, there are few reports on economically reusing N$_2$O from flue gas by direct oxidation method, which would have great social and economic benefit potentially applied in adipic acid production and nitric acid industries [18-20]. Bechtold et al. [21] proposed a method of removing NO from waste gas by using the reaction between NO and O$_3$, and the mixture could be used to produce nitric acid by suitable operation. Whelan [22] put forward a catalytic method which could effectively oxidize NO to NO$_2$ at the temperature of 100–400°C in the presence of excess oxygen. Zhou et al.[23]...
proposed a method dealing with NO contained in exhaust by using a kind of difunctional catalyst with high activity at low-temperature, where NO was converted to NO₂, in which the molar ratio of oxidant with NO is about 0.5~1.2:1. Therefore, nitric acid would be produced and the concentration of NO₂ in exhaust was less than 15ppm after treatment. Other N₂O reusing technologies from adipic acid production processes and nitric acid industry, such as purification, production of phenol and oxidation of aromatic compounds, etc., also face great challenges and economic constraints. Therefore, the suitable technology of effectively controlling N₂O emission is urgent, which should be able to meet the industrial need and also bring certain economic benefit on offsetting cost used for the pollution controlled operation [24-28].

This paper proposed a novel catalytic system for exhaust gas N₂O removal by catalytic oxidation method, in which N₂O could be selectively converted to the mixture of NO and NO₂ under suitable reaction conditions, which could be potentially used to produce nitric acid. It could be an economic method of reusing N₂O applied in adipic acid production and nitric acid industries.

2. Experimental

2.1. Sample preparation
Catalysts used in this study were prepared by co-precipitation method. The conductivity of deionized water used is normally in the range of 1 to 2μs/cm. The salt solution containing suitable catalytic precursor was prepared in certain concentration and used in the next step (solution A). Similar method was used to prepare alkali solution (solution B). Afterwards, the catalyst was prepared by titration method. Firstly, certain amount of solution B was transferred to a four mouth flask under reflux and appropriately stirring speed. The temperature was controlled between 60~90℃. Then, certain amount of solution A and B was transferred to two dropping funnels, respectively. The solution A was titrated into the four mouth flask with the speed of 30~90 drops/min and solution B was used to control pH value in the range of 9.0 ~ 10.0 during the titration process. The colloidal precipitation was continuously obtained during the process of titration, which was crystallized for 10~24 hour in the oven under 60 ~ 90℃. Afterwards, the precipitation was repeatedly washed and filtered with deionized water until pH for the washing solution was between 8.0 ~ 9.0. Finally, the precipitation was dried in the oven and calcined in the muffle furnace through temperature programming method, respectively.

2.2. Characterization
BET characterization was performed on ASAP 2020 surface and pore structure analyzer (Micromeritics Corporation, USA). The particle size distribution for the catalyst precursor prepared by titration was characterized by using Mastersizer 2000 laser particle size analyzer (UK). Infrared spectroscopy characterization was performed on Nicolet NEXUS 470 (USA), DTGS detector, scanning number, 32 times, and resolution, 4cm⁻¹. Infrared reaction tank was manufactured by Xian Quan factory (Tianjin, China). Samples were also characterized by using TG/DTA 6300 analyzer (Takara Corporation, Japan). Basic test conditions: N₂ flow rate of 40ml.min⁻¹, temperature range of 10~850℃ with increasing rate of 20℃/min.

2.3. Experimental setup
The system used for catalyst performance evaluation was a self-designed micro laboratory reactor, which mainly included feeding, flow steady controlling, electric controlling, reaction and measuring parts, respectively. Mainly, the feeding part included 4 sets of independent intake lines in order to study the catalyst performance under different gas composition. The flow steady part included units of intake controlling, safety valve and pressure, etc. The reaction part included preheating and heating furnace, reactor, temperature control and automatic recording devices. Specially, the reaction part included two sets of independent stainless steel reactors, in which one reactor was under operation while the other was being prepared at the same time. The reactor exit was connected with a cooler and
the gas mixture was discharged through the back pressure valve and cumulatively recorded by the metal rotameter.

2.4. Analysis methods

2.4.1. Chromatography. $N_2O$, $N_2$ and $O_2$ were analyzed by gas chromatography GC-2010 PLUS (Shimadzu) using 5A molecular sieve and Porapak Q packed column, respectively, and TCD detector. Basic conditions: helium (99.999%) as carrier gas with flow rate of 30ml.min$^{-1}$, column pressure 0.12MPa, column temperature 45$^\circ$C, detector temperature 150$^\circ$C, bridge current 140mA.

2.4.2. Titration. NO$_2$ in exhaust could be directly absorbed while NO must react with $O_2$ in order to form HNO$_3$. Thus, certain amount of H$_2$O$_2$ was added in the absorption liquid in the process of chemical analysis in order to ensure complete NO conversion. The following equation was used to calculate NO$_x$ (NO$_2$+NO) concentration in the liquid.

$$NO_x(mol\%) = \frac{8.313 \times C_{HCl} \times (273 + t) \times (V_{w} - V_{o}) \times 100}{P_{o} \times (V_{w} - V_{H_2O})}$$

Where, $C_{HCl}$ - concentration of standard HCl solution, mol.l$^{-1}$, $P_{o}$ - standard atmospheric pressure after corrected to 0$^\circ$C, KPa, $t$ - titration temperature, $^\circ$C, $V_{w}$ - consumption amount of standard HCl in blank titration, ml, $V_{o}$ - consumption amount of standard HCl in titration of the absorbed liquid sample, ml, $V_{w}$ - volume of vacuum bottle, ml, and $V_{H_2O}$ - volume of vacuum bottle containing H$_2$O, ml.

2.5. Definition of catalyst’s activity and selectivity

The catalyst’s activity on $N_2O$ conversion and selectivity on production of NO$_2$ and NO could be defined according to the composition of $N_2O$, NO and NO$_2$ both in inlet and exit in the exhaust, respectively. Assuming $k_1$ - the molar composition of $N_2O$ in exhaust analyzed by gas chromatometry, $k_2$ - the molar composition of NO$_2$ in absorbed liquid analyzed by titration.

$$x = \frac{1}{1 + 0.5 \times (k_1 + k_2)} \frac{P}{RT} \left[ V_m(N_2O) - (k_1 + k_2) \left( V_m(O_2) + V_m(\text{others}) + V_m(N_2O) \right) \right]$$

$$y = \frac{k_1}{2 + (k_1 + k_2)} \frac{P}{RT} \left[ V_m(N_2O) + 2 \left( V_m(O_2) + V_m(\text{others}) + V_m(N_2O) \right) \right]$$

$$z = \frac{k_2}{(1 + 0.5 \times (k_1 + k_2)) \times (2 + (k_1 + k_2))} \frac{P}{RT} \left[ V_m(N_2O) \left( 1 + 0.5(k_1 + k_2) \right) + V_m(O_2) + V_m(\text{others}) + V_m(N_2O) \right] \left( 2 + (k_1 + k_2) \right)$$

Therefore, the catalyst’s activity and selectivity was calculated according to the following equations, respectively.

$$\text{Activity} = \frac{x + z}{x + y + z} \times 100\%$$

$$\text{Selectivity} = \frac{z}{x + y + z} \times 100\%$$
3. Results and Discussion

3.1. Characterization

The specific surface area, average pore size and pore capacity for prepared catalysts show that the specific surface area is 95~140 m²/g, average pore size is 8~12 nm and total pore capacity is 0.25~0.35 cm³/g, respectively.

Catalysts prepared by co-precipitation method maybe somewhat have a similar structure of hydrotalcite before calcination, while the prepared precursor would lose part or all of the similar hydrotalcite structure after calcination at different temperature, which has been characterized by FT-IR for both before and after calcination, respectively. FT-IR characterization on Zr-Mg-Al-O sample before calcination indicated that the characteristic peak appeared at 3400 cm⁻¹, 1630 cm⁻¹, 1350 cm⁻¹, 750 cm⁻¹, 630 cm⁻¹, 530 cm⁻¹ and 430 cm⁻¹, respectively. Combining with FT-IR standard data and related information, peak at 3400 cm⁻¹ was attributed by stretching and bending vibration of the water molecule between layers. Peak at 1600 cm⁻¹ belonged to bending vibration of OH⁻ of the crystal water, while it moved towards the lower wave position when compared to free state OH⁻, whose peak is at 3600 cm⁻¹. It could be because of the interaction among H₂O, CO₃²⁻ or OH⁻ in the layer. Peak at 1350 cm⁻¹ belongs to the asymmetrical stretching vibration of C-O in the structure of CO₃²⁻, which implied there was CO₃²⁻ ion existing in the layer. However, compared with the peak of CO₃²⁻ in FT-IR standard data (1430 cm⁻¹), it indicated that the peak of CO₃²⁻ in the hydrotalcite-like-structure already moved towards lower wave number, which indicated there might be hydrogen bonding interaction between water molecule and CO₃²⁻ in the layer. Peak at 700 cm⁻¹ to 400 cm⁻¹ was attributed by the presence of metal oxide M-O, which showed the Zr-Mg-Al-O catalyst precursor prepared by coprecipitation method emerged the hydrotalcite-like structure before calcination. Similar results were obtained for other catalyst precursors prepared by coprecipitation method. FT-IR characterization of Zr-Mg-Al-O sample after calcination indicated that its characteristic peaks were similar with its precursor, which implied that the calcined sample somehow remained its hydrotalcite-like-structure when the calcination temperature was at 580 °C. Meanwhile, it showed the peak at 1600 cm⁻¹ on FT-IR was obviously weakened. It indicated that the crystal water in the calcined sample already greatly decreased after calcination. Peak at 1350 cm⁻¹ was also weakened, which indicated the CO₃²⁻ ion in the calcined sample also decreased. Therefore, FT-IR characterization showed some common properties for Zr-Mg-Al-O before and after calcination under experimental condition, however, its microstructure and composition had already undergone much variation.

TG/DTA characterization of Zr-Mg-Al-O before calcination indicated here were two obvious weight loss peaks at about 200 °C and 380 °C, respectively. The peak at temperature lower than 200 °C belonged to the loss of interlayer and physical adsorbed water in hydrotalcite-like-structure. The weight loss from 200 °C to 380 °C belonged to interlayer water removal, while the weight loss from 380 °C to 600 °C was caused by OH⁻ removal as well as decomposition of CO₃²⁻ and NO₃⁻. The curve of weight loss became stable when the temperature was above 600 °C, which was consistent with TG/DTA characterization of hydrotalcite-like-structure reported in reference [25]. TG/DTA analysis of Zr-Mg-Al-O calcinated at 580 °C indicated that it has no obvious weight loss peak in the whole temperature range compared with sample before calcination. This implied that most of the OH⁻, CO₃²⁻ and NO₃⁻ ions in the sample of Zr-Mg-Al-O have been removed after calcination.

3.2. Catalyst’s performance in fixed-bed reactor

The variation of N₂O conversion ratio with temperature was shown in Figure 1 for Ce-Mg-Al-O, Mn-Mg-Al-O, Zr-Mg-Al-O, Pt-Cu-Zn-O and Pt-Zr-Zn-O catalysts, and the selectivity of NO production was shown in Figure 2, respectively. The basic experimental condition in the study was 40%(v)N₂O+40%(v)N₂+20%(v)O₂ as feed material, hourly space velocity of 3000 h⁻¹, 0.1 MPa of system reaction pressure, respectively. It could be seen from Figure 1 that conversion ratio of N₂O increased with reaction temperature, while activities for the different catalysts did not show much
difference under the experimental conditions. The selectivity, shown in Figure 2, was quite different under experimental conditions. The sequence of catalyst performance on NO selectivity could be Pt-Zr-Zn-O > Pt-Cu-Zn-O > Zr-Mg-Al-O > Mn-Mg-Al-O > Ce-Mg-Al-O, respectively. Therefore, the idea of designing catalyst based on theoretical calculation of mental acid-base strength and the mechanism of N₂O catalytic reaction was successful. Furthermore, the selectivity performances of Pt-Cu-Zn-O and Pt-Zr-Zn-O catalysts were both improved under experimental condition, which led to more than 10% and 15% on NO production under the temperature range of 550°C to 650°C, respectively. It was a promising result to apply this method for N₂O reuse in adipic acid production and nitric acid industry.

![Figure 1. N₂O conversion performed on catalysts prepared by co-precipitation method](image1)

![Figure 2. Selectivity of NO production performed on catalysts prepared by co-precipitation method](image2)
4. Conclusions
A series of catalysts used to control N₂O emission and potentially produce nitric acid as by-product have been designed according to the acid-base strength theory of metal oxides and prepared by co-precipitation method. The basic properties of the catalysts have been characterized by multiple methods such as BET, laser particle size analyzer, FT-IR and TG/DTA. The catalysts’ performance have been evaluated in a fixed-bed reactor with 40%(v)N₂O+40%(v)N₂+20%(v)O₂ as feed material, 3000h⁻¹ space velocity and 0.1MPa system pressure. The sequence of catalyst performance on NO was Pt-Zr-Zn-O > Pt-Cu-Zn-O > Zr-Mg-Al-O > Mn-Mg-Al-O > Ce-Mg-Al-O. The selectivity of Pt-Cu-Zn-O and Pt-Zr-Zn-O catalyst for NO production was more than 10% and 15% in the temperature range of 550°C to 650°C, respectively. The basic experimental results show that it is a promising method to be applied for N₂O reuse in adipic acid production and nitric acid industry, and also provide the basis for further relative theoretical and experimental studies.

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