Ammonia Concentration Measurement by Catalytic Oxidation*

Sanyo TAKAHASHI** and Iwao YAMASHITA**

An ammonia converter was constructed using a commercially available platinum catalyst, with the aim of applying it for the measurement of ammonia concentrations. The dependence of the ammonia converter efficiency on the reaction temperature and the ammonia concentration was investigated by measuring the concentration of the converted nitric oxide. The results showed that the catalyst almost completely oxidized ammonia into nitric oxide at temperatures above 600°C in the tested range of ammonia concentrations. In addition, by combining the ammonia converter with a chemiluminescent NO_x analyzer we were able to measure the ammonia concentration in an ammonia-nitric oxide mixture to an accuracy of within 3% by making a correction due to the oxygen concentration.

Key Words: Catalyst, Pollutant, Measurement, Ammonia, Converter, Nitric Oxide, Ammonia Concentration Measurement

1. Introduction

At power generation plants or incineration plants, ammonia is used with or without a catalyst to reduce NO in the exhausted gas. Because of such practical applications, extensive studies on ammonia oxidation and NO-NH₃-O₂^{(1)~(4)} reaction processes are being conducted. However, these reaction processes are not fully understood yet. As these studies progress, a more efficient ammonia DeNox system is expected to be developed in the future. Recently, a study of the spark ignition engine⁽⁵⁾, which is fuelled with an ammonia-hydrogen mixture generated from the partial decomposition of ammonia, has been undertaken as an approach to the hydrogen energy utilization.

Both theoretical studies and practical applications necessitate a diagnostic tool capable of continuously analyzing ammonia in the exhausted gas, with-

out the interference of H₂O and NO, in order to investigate the reaction process or to monitor the concentration of ammonia carried over. Ammonia concentrations are measured mainly by gas chromatograph and wet methods⁽⁶⁾, such as absorptiometry and acid-base titration, however, these analyzers are unable to be used for continuous measurement. On the other hand, the NDIR⁽⁷⁾ and a new analyzer utilizing the reduction reaction of NO by NH₃ in the presence of O₂, are commercially available for continuous ammonia analyses. However, the former possesses the undesired characteristic of interference from H₂O and the latter can not be used for measuring ammonia concentrations which are higher than NO concentrations.

Hardy and Knarr⁽⁸⁾ proposed a new technique in which the ammonia concentration is obtained by measuring the concentration of the NO with a chemiluminescent NO_x analyzer after converting the ammonia into NO with a catalyst; they subsequently proved it to be useful for the measurement of ammonia concentration. They used an expensive platinum mesh as the catalyst and obtained an ammonia conversion efficiency of close to 100 % at reaction temperature above 600°C. Also, they set the pressure of the

* Received 6th January, 1989. Paper No. 88-0075 B

** Energy Engineering Department, Mechanical Engineering Laboratory, Agency of Industrial Science and Technology, MITI, 1-2 Namiki, Tsukuba, Ibaraki, 305, Japan

reactor below 10 kPa in order to avoid rapid poisoning of the catalyst, which occurs at atmospheric pressure. While these facts suggested that the selection of the catalyst and the determination of the reaction conditions were important for the construction of an ammonia converter, they did not mention the possibility of catalysts other than the platinum mesh and gave no description of the details of the reaction conditions, for example, packed quantity of the catalyst and space velocity (SV value). Then, Lucas and Brown⁽⁹⁾ applied this technique to the study of NO-NH₃-O₂ reaction.

In the present study, an ammonia converter was constructed according to the technique proposed by Hardy and Knarr using a commercially available platinum catalyst. The influences of the reaction temperature and ammonia concentration on the conversion efficiency, and the interference between ammonia and NO were investigated by measuring the NO_x concentration with a chemiluminescent NO_x analyzer. Based on these experimental results, the performance of the catalyst was assessed. Also in this paper, discussions of several points to be taken into consideration when employing the combination of the ammonia converter and a chemiluminescent NO_x analyzer as an ammonia analyzer are presented.

2. Structure of the Ammonia Analyzer

Figure 1 shows the structure of the ammonia analyzer used in this study. The sample gas, which is aspirated through a dry vacuum pump, reaches a 3-way valve after flowing through a filter and a PTFE capillary tube. The 3-way valve enables the sample gas to bypass the ammonia converter. This analyzing system has two different measurement modes which are labelled the NO_x mode and the ammonia mode. In the former mode, the NO_x concentration is measured, while in the latter mode the NO_x + ammonia concentration is measured. The flow rate of the sample gas is set to about 500 Ncm³/min by adjusting the length of the capillary tube. Also, the pressure in the ammonia converter is set below 10 kPa to avoid poisoning of the

Fig. 1 Structure of the ammonia converter

catalyst. The sample gas is then dehumidified by an electronic cooler, the temperature of which is kept below 2°C, and a small quantity of the gas is introduced to the chemiluminescent NO_x analyzer. The NO_x analyzer has been improved so that not only the NO, but also the NO_x concentration can be measured by making a bypass of the NO_x converter. Every component in this system is jointed to the other with PTFE tubes of 4 mm inner diameter and stainless steel fittings.

The ammonia converter consists of a quartz reaction tube packed with the catalyst and an electric furnace to maintain the constant temperature of the reactor. The reaction tube is U-shaped and the inner diameters of the inlet and outlet tube are 5 mm and 10 mm, respectively. As shown in Fig. 2, the granular platinum catalyst (3 mm in diameter; Engelhard DASH-220) fills the lower portion of the outlet tube for a length of 135 mm. The catalyst is fixed with quartz wool at the top and bottom. Here, the space velocity is estimated to be around 3 000 h⁻¹. The sample gas enters the catalyst bed after being preheated in the inlet tube, and the ammonia contained in the gas is converted into NO in the presence of O₂. The test gas is supplied from NO standard gas, ammonia standard gas (both are N₂-balanced), N₂ gas and O₂ gas cylinders. Their flow rates are regulated with mass flow meters. The initial concentrations of NO(=[NO]_T) and ammonia(=[NH₃]_T) are calculated from these flow rates and the standard gas concentrations. Since the uncertainty of the flow rates is reduced to 0.5% by calibrating the mass flow meters, and the same standard gas cylinders are used throughout the experiments, the scatters in [NO]_T and [NH₃]_T obtained in this way are below 1%.

Fig. 2 Detailed drawing of the catalytic reactor

3. Experimental Results

The ammonia analyzer should possess the following performance characteristics. The first is linear sensitivity for ammonia concentration. When an ammonia converter is employed, the conversion efficiency must be constant regardless of the ammonia concentration level. The second is not to interact with the other constituents, which demands that the ammonia be converted selectively into NO by the catalyst. The third concerns the oxidation of the converted NO into NO₂ during the sampling, as is seen in the standard measurement method of NO. Usually, NO₂ is readily adsorbed onto the tube wall, the converter and the parts making up the NO_x analyzer. This causes a lowering of the measurement accuracy for the NO concentration, which in turn lowers the accuracy for the ammonia concentration. The performance of the ammonia converter is examined from the points of view described above.

3.1 The effect of the oxygen concentration on the measurement of NO_x concentration

In this technique, the measurement of the ammonia concentration is made by converting the ammonia into NO and measuring the converted NO concentration. Therefore, it is important to know in advance the effect of the oxygen concentration on the accuracy of the NO concentration measurement. In order to clarify the effect of the oxygen concentration, NO and NO_x concentrations were measured in both the NO_x mode and ammonia mode adding oxygen from 0 to 10% to the N₂-balanced NO flow (no ammonia was added). The experimental results are shown in Figs. 3 and 4. The abscissa shows the oxygen concentration, and the ordinate represents the ratios of the measured NO concentration ($=[\text{NO}]_M$) and the measured NO_x concentration ($=[\text{NO}_x]_M$) to the initial NO concentration ($=[\text{NO}]_T$). The measurements were made while varying $[\text{NO}]_T$ in the range of 100 to 470 ppm. Since the measured values show little dependency on the NO

concentration level, they are represented by a circle in Fig. 3 and by a circle with an intersecting vertical line in Fig. 4.

In Fig. 3, $[\text{NO}]_M$ diminishes linearly with an increase in the oxygen concentration, while $[\text{NO}_x]_M$ does not become invariant and shows a slight decrease compared to $[\text{NO}]_M$. Thus, the oxidation of NO into NO₂ is enhanced with an increase in the oxygen concentration, and some of the NO₂ is adsorbed onto the walls of the tubes or onto the parts of the NO_x analyzer. The same trend can be seen in the ammonia mode (refer to Fig. 4). In this case, however, the quantity of NO oxidized to NO₂ is much larger and is three times that of the NO_x mode. Taking into consideration the differences in the flow path between the NO_x and the ammonia mode leads to the estimation that about 70% of the total NO₂ is formed at the ammonia converter in the ammonia mode. Regardless of $[\text{NO}]_T$, the values of $[\text{NO}]_M/[\text{NO}]_T$ and $[\text{NO}_x]_M/[\text{NO}]_T$ plotted against the same O₂ concentration are constant with an error of 1%. Consequently, the NO concentration of the sample gas can be measured accurately by correcting $[\text{NO}]_M$ or $[\text{NO}_x]_M$ for the oxygen concentration.

3.2 The efficiency of the ammonia converter

The efficiency of the ammonia converter has a large dependency on the reaction temperature as well as the space velocity. By varying the reactor temperature in the range of 200°C to 750°C, the measurements of the conversion efficiency were made for the mixture containing 400 ppm NH₃, 10% O₂ and 90% N₂ (no NO is contained). Its dependency on reaction temperature is shown in Fig. 5. The conversion efficiency was defined as the ratio of the measured NO_x concentration ($=[\text{NO}_x]_M$) to the initial NH₃ concentration ($=[\text{NH}_3]_T$). As can be seen in Figs. 3 and 4, this analyzing system does not give an accurate concentration of NO_x because of the adsorption of NO₂, though there exists no problem in investigating the relative dependency. The conversion efficiency attains a constant

Fig. 3 Influence of O₂ concentration on NO_x concentration measurement in NO_x mode

Fig. 4 Influence of O₂ concentration on NO_x concentration measurement in ammonia mode

value above 600°C after a sharp rise around 300°C, and the platinum catalyst used in the ammonia converter is sintered at the temperature above 800°C. Accordingly, it is recommended for the efficiency and the durability that the catalyst be used in the temperature range of 600°C to 800°C. In the following experiments, the temperature of the reactor has been set at 600°C ± 10 .

The dependency of the conversion efficiency on the oxygen concentration was also investigated by adding 2~10% oxygen to ammonia (no NO was added). Three concentrations of ammonia in the range of 100 ppm to 435 ppm were employed for testing. The experimental results are shown in Fig. 6. Although the measured values of NO and NO_x indicate a scatter of around 2% depending on the ammonia concentration level, which results in the lowering of measurement accuracy for ammonia concentration, the values diminish with almost the same slopes shown in Fig. 4 for the increase in the oxygen concentration. By making correction for the O₂ concentra-

tion, it is possible to measure the ammonia concentration with an error of 2%.

In Fig. 6, the conversion efficiency is found to be in excess of 1 by 2% or more at low concentrations of O₂. This difference is excessive when compared to the error estimated from the accuracy of the NO_x analyzer and the measurements of the flow rates. Also, it seems unlikely that NO_x is formed from constituents other than NH₃. In addition to the measuring errors described above, the uncertainty involved in the ammonia concentration in the standard gas cylinder is a probable cause for such a large difference, because its accuracy, certified by the standard gas maker, is 2%. The real ammonia concentration in the standard gas is considered to be lower than the nominal one.

Since the conversion efficiency shown in Fig. 6 is only apparent, the O₂ concentration correction must be made for the measured value of NO or NO₂ in order to obtain the real efficiency. The characteristics of NO oxidation into NO₂ may be different from the one in Fig. 4, because the formation of NO takes place at the ammonia converter. However, as described before, NO is oxidized mainly in the ammonia converter. Therefore, the measured values can be corrected according to the oxidation characteristics shown in Fig. 4. The conversion efficiency corrected in this way becomes a constant, which leads to the conclusion that the actual conversion efficiency has little dependency on the O₂ concentration.

3.3 Effect of NO on the measurement of the ammonia concentration

When using the ammonia converter on a sample gas containing ammonia, NO and O₂ attention must be paid to the catalytic reduction of NO by ammonia and the precision of the measurement for the ammonia concentration. In order to clarify this, the measurements of NO and NO+NH₃ concentrations were performed on the mixtures at two different concentration ratios of NO to ammonia. The concentration ratios of 1 and 3 were employed for the experiments.

Figure 7 shows the variation of the NO concentration measured in the NO_x mode against the O₂ concentration. The scatter of the measured values for each O₂ concentration is small regardless of the ratio of NO to the ammonia concentration. For comparison, the experimental result of the sample gas for NO only is also shown in Fig. 7 by a broken line. No significant discrepancy can be seen between them. On the other hand, a small reduction of NO by ammonia was observed to take place in the NO_x converter which invalidates the linear correction due to the O₂ concentration. This, in turn, results in the lowering of the accuracy for the measurement of the NO concentration.

Fig. 5 Dependence of the conversion efficiency on reactor temperature

Fig. 6 Influence of O₂ concentration on ammonia concentration measurement

The NO_x concentrations measured in the ammonia mode are shown in Fig. 8. They diminish linearly against the O_2 concentration. The solid line and broken line represent the $\text{NO}_x + \text{NH}_3$ concentrations which are predicted from Fig. 4 and Fig. 6, respectively. They show good agreement with the NO_x concentrations measured with the coexistence of NO and ammonia. These experimental results indicate that the ammonia is converted into NO almost completely, without interference from NO. While a similar behavior is observed when the measurement is carried out on the NO concentration, it is favorable for the measurement accuracy of ammonia concentration to use NO_x , which has a smaller number of corrections than NO.

The experimental results described above also mean that the concentration of ammonia coexisting with NO can be measured with a reliable accuracy if the measured values are corrected for the O_2 concentration according to the calibration formulae obtained separately using the NO and NH_3 standard gases. Figure 9 shows the relative errors of the measured concentrations of NO and ammonia, which were corrected in this way, compared to their initial concentrations.

From Fig. 9, this analyzing system is found to be

Fig. 7 NO concentration measurement under coexistence of ammonia and NO

Fig. 8 $\text{NH}_3 + \text{NO}$ concentration under coexistence of ammonia and NO

able to measure NO concentration with an error below 1%. On the other hand, the error for the measurement of the ammonia concentration increases to 1.5% in the case of $[\text{NO}]_T/[\text{NH}_3]_T=1$ (denoted by circles) and to 3% in the case of $[\text{NO}]_T/[\text{NH}_3]_T=3$ (denoted by triangles). In this system, the concentration of ammonia is obtained by subtracting the measured value of NO for the NO_x mode from the NO value of the ammonia mode. Therefore, the higher the NO concentration is compared to the ammonia concentration, the more the measuring accuracy of the latter is affected by that of the former.

4. Discussions

Some problems remain unsolved for utilizing this analyzing system in the measurement of concentration of ammonia in actual burned gas. One of the problems is water. Since ammonia gas easily dissolves in water and a large amount of water vapor causes errors during the measurement of NO_x concentration, it is necessary to dehumidify the burned gas. The ammonia is oxidized into NO in the ammonia converter. Therefore, by heating the flow path between the sampling tube and the converter and by installing another dehumidifier between the converter and the vacuum pump to avoid the condensation of water vapor in the vacuum pump, the combustion gas can be dehumidified without the dissolution of ammonia gas into water.

The burned gas is composed of NO_2 as well as NO, which brings about another problem. In this analyzing system, some of the NO_2 is adsorbed onto either the tube wall or the elements consisting of the NO_x analyzer during the sampling, which makes it difficult to measure distinctively the original concentrations of NO and NO_2 . In this study, PTFE tubes and stainless steel fittings were employed to prevent the adsorption of NO_2 . Besides the piping and fittings, the vacuum pump, the dehumidifier and the catalyst for the NO_x converter must suppress the adsorption of NO_2 . In particular, the catalyst of the NO_x converter must possess a high conversion efficiency, be inactive to the reduction of NO by ammonia, and not adsorb NO_2 .

Fig. 9 Measurement accuracy for NO and ammonia under coexistence of ammonia and NO

The final problem discussed here is the durability of the ammonia converter catalyst. In this study, the pressure of the ammonia converter was set below 10 kPa according to the technique proposed by Hardy and Knarr in order to prevent the poisoning of the catalyst. Previously, the catalyst was used for more than 50 hours with no deterioration observed. Accordingly, there appears no problem in using it in laboratories. As the performance test has not yet carried out under atmospheric pressure, no judgement can be given as to whether the catalyst is poisoned or not under high pressures. If a catalyst that is strongly resistant to poisoning can be found, then it will be easier to choose the vacuum pump and the dehumidifier.

5. Conclusions

According to the technique proposed by Hardy and Knarr, an ammonia converter was constructed using a commercially available platinum catalyst. The influence of the reaction temperature and the ammonia concentration on the conversion efficiency, and the interaction between NO and ammonia were investigated by measuring the concentration of NO and NO_x using a chemiluminescent NO_x analyzer. Also, based on the experimental results, assessment of the performance of the analyzing system, consisting of the ammonia converter and the chemiluminescent NO_x analyzer, was carried out. As a result, the following conclusions have been reached.

(1) In the presence of O₂, the catalyst employed (Engelhard Dash-220) completely oxidized ammonia into NO at reaction temperatures above 600°C without the interaction of NO and ammonia.

(2) For achieving a good precision for the measurement of NH₃ concentration, it is necessary to know the oxidation characteristics of NO, since a considerable quantity of NO is oxidized into NO₂ in

the ammonia converter.

(3) The combination of the ammonia converter and chemiluminescent NO_x analyzer was found to be capable of measuring the ammonia concentration in the ammonia-NO mixture with an error of 3% after correcting for the oxygen concentration.

We would like to express our appreciation to Mr. Katsuhiko Takahashi, a student of Kougakuin University, for his assistance with this study.

References

- (1) Muzio, L. J., Arand, J. K. and Teixeira, D. P., Gas Phase Decomposition of Nitric Oxide in Combustion Products, Proc. 16 th Symp. Int. on Combust., (1976), p. 199.
- (2) Dean, A. M., Hardy, J. E. and Lyon, R. K, Kinetics and Mechanism of NH₃ Oxidation, Proc. 19 th Symp. (Int.) on Combust., (1982), p. 97.
- (3) Yoshikawa, N., Nagano, S. and Ohtake, K., Trans. Jpn. Soc. Mech. Eng. (in Japanese), Vol. 50, No. 452, B (1984), p. 1095.
- (4) Kimball-Linne, M. A. and Hanson R. K., Combustion-Driven Flow Reactor Studies of Thermal DeNO_x Reaction Kinetics, Combust. Flame, No. 64 (1986), p. 337.
- (5) Nedachi, O. and Korematsu, K., Proc. Jpn. Soc. Mech. Eng., (in Japanese), No. 874 (1987), p. 337
- (6) Takagi, T., Formation Mechanism and Controls of Pollutants in Combustion System, (in Japanese), Jpn. Soc. Mech. Eng., p. 224.
- (7) Hori, M., Formation Mechanism and Controls of Pollutants in Combustion System, Jpn. Soc. Mech. Eng., (in Japanese), p. 226.
- (8) Hardy, J. E. and Knarr, J. J., Technique for Measuring the Total Concentration of Gaseous Fixed Nitrogen Species, J. Air Pollut. Assoc., 32-4(1982), p. 376.
- (9) Lucas, D. and Brown, N. J., Characterization of the Selective Reduction of NO by NH₃, Combust. Flame, No. 47(1982), p. 219.