

燃料 過濃/稀薄 調節의 觸媒燃焼에 의한 Fuel-NOx 低減 技術

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Reducing technology of fuel-NOx generation using fuel-rich/-lean catalytic combustion

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ABSTRACT

A two-step fuel-rich/fuel-lean catalytic combustion seems to be one of the most effective methods to control simultaneously the NO generation and the hydrocarbon (HC) conversion from fuel-bound nitrogen. By controlling equivalent air ratio for maintaining fuel-rich and fuel-lean condition over each catalytic layer, space velocity, inlet temperature, and catalyst component, the HC and ammonia conversion efficiency higher than 95% could be achieved, with ammonia conversion to NO remaining below 5%. The experimental results would be applied to the combustion of land fill gas and to gasified refuse-derived fuels as a method of minimizing NO generation.

Key Words : Fuel-NOx; 2-step catalytic combustion; low BTU gas; Ammonia; Biomass

1. Introduction

Conversions of biomass, coal and some waste materials by gasification offer an opportunity to utilize such fuel sources cleanly. The need for clean and efficient power production processes requires development of processes based on gasification technology. In principle, during gasification and gas cleaning, it is possible to remove several precursors of noxious gas in post-combustion emission. Introducing gasification would also make possible to design more efficient processes for the solid fuels, such as Integrated Gasification Combined Cycle (IGCC) [1]. Such systems could have efficiencies over 70%, in comparison with 34% for conventional coal-fired power stations [2]. To use the solid

fuels as a clean fuel, sulfur emissions could be lowered substantially by using an adequate technology [3]. Another approach to promote the formation of N₂ by limiting the availability of oxygen during oxidation of the light volatiles containing NH₃ was studied in gasification process [4].

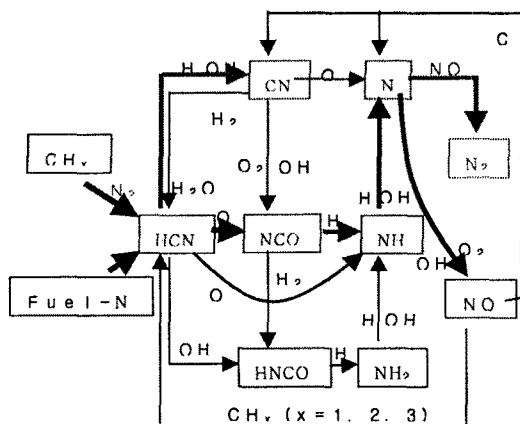
The oxidation of ammonia either under high-temperature conditions (flames, shock tube) or during fuel-lean oxidation at moderate temperatures (flow reactor) has been extensively studied in the past. As shown in Figure 1, Glassman [5] summarized the fuel-nitrogen conversion at high-temperature flame condition. Formation of various nitrogen-bearing species during this process depends on atmospheric conditions in the combustor. Acceleration of NO formation by nonequilibrium radicals appears to be more important in diffusion or low-pressure premixed flames and in stirred reactors under lean conditions, accounting for up to 80% of the total NO formation.

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[Fig. 1] NO_x formation pathways in combustion process

When burning the biomass in a fluidized bed or on a grate in a reducing environment, initial conversion of the volatiles of biomass occurs at moderate temperatures. Glarborget al. [6] proposed the pathways for formation of N₂ and NO from inlet NH₃ at moderate temperatures and under fuel-rich conditions. Brink [7] predicted that a single method of equivalent air ratio control in the absence of reductive gases was less effective to reduce NO formation from NH₃. In addition, Skreiberg et al. [8] reported that the gas-phase volatile nitrogen in flames was sequentially stripped of carbon and hydrogen, and the oxidation selectivity towards NO and N₂ was largely determined by the competition between reactions of N atoms with OH/O₂ (to form NO) and with NO (to form N₂). With the two proposed mechanisms of selective NH₃ conversion at fuel-lean conditions [5] and fuel-rich states [8], it can be deduced that the ammonia conversion to N₂ may occur in the presence of NO, and more effectively in the presence of reductive gases.

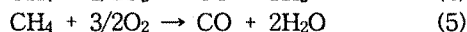
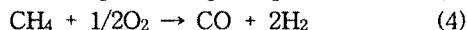
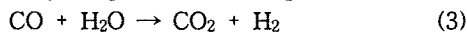
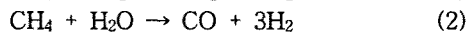
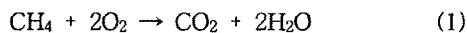
Amblard et al. [9] reported that Ni catalyst supported on Al₂O₃ was effective for the selective conversion of NH₃ to N₂ in the presence of excess O₂. Nevertheless, in the same article it was also reported that Mn/Al₂O₃ and Fe/Al₂O₃ were more active than Ni/Al₂O₃, possibly because of the enhanced redox properties.

Kusar et al. [10] have shown that the Pd-based catalysts were the most active both

for the gasified waste, i.e. refuse derived fuels (RDF) and for methane in catalytic combustion. Incorporating an active support such as LaMnAl₁₁O₁₉ enhanced the catalytic activity for methane in gasified waste. Substituting Mn into the crystal lattice of the spinel also increased the catalytic activity for H₂ and CO, while the methane activity remained low. The metal oxide catalysts also showed a higher selectivity for conversion of NH₃ into N₂ than the catalysts containing precious metals. The Pd/LaMnAl₁₁O₁₉ catalyst showed the highest activity for combustion of the synthetic gasified waste; H₂ ignited first, immediately followed by CO at 200°C. Generally the oxidation of NH₃ followed CO and H₂ over the precious metals showing high conversion into NO under fuel-lean condition.

Witton et al. [11] examined a high-pressure catalytic combustion of low heat value fuels. In their experiments on catalytic combustion, reaction-specific catalysts were used to minimize rates of ammonia conversion to NO, thereby permitting acceptance of high levels of ammonia in the fuel gas without the disadvantages of waste disposal and thermodynamic loss to the engine cycle. By using Rh catalysts at temperatures between 600 to 700°C, ammonia conversion of the order 35~40% was obtained with low CO/H₂ content in the fuel, in the sample gas at the post-catalyst section [11].

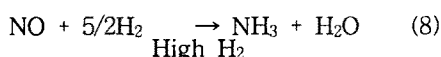
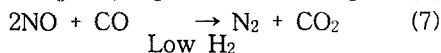
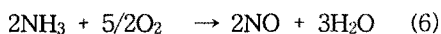
Equilibrium composition of partial and complete oxidation was modeled on the basis of following equations [12, 13]:



Calculations have shown that even under fuel-rich conditions, a part of methane could be completely oxidized. At a high temperature, the endothermic reaction (2) might be taken place in parallel with the exothermic reactions (3~5).

Following equations (6~8) describe possible conversion of NH₃ and NO in a mixture of CO, H₂, NH₃, NO, and N₂ [11]. According to

some reports [5, 14], the reaction time in the isothermal region is considerable, ranging from more than 4s at the lowest temperature of 430°C to about 1s at the highest temperature of 1000°C, the reaction being initiated at about 420°C. Ammonia and nitric oxide conversion increased with temperature, with conversion rates comparable in magnitude.



However, the reaction time for ammonia conversion to N_2 was too long to influence the results in real combustion system. Also, it should be noted that the reaction paths dominating under fuel-rich conditions are significantly different between flow reactors and fuel-rich flames.

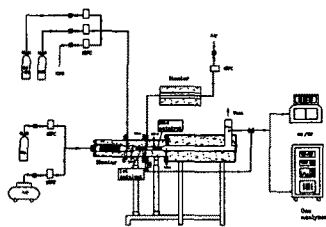
The stepwise catalytic burner described in this work aims to minimize NO generation that results from NH_3 oxidation. Thus, the 1st catalyst utilizes to achieve a superior conversion of NH_3 to N_2 at low temperature and at short reaction time under fuel-rich condition. In the 2nd catalyst, NO generated in the 1st catalyst is reduced by the reductive gases decomposed from methane in the 1st catalyst [see equation (7)]. At the same time, the remaining reductive gases including methane fuel-lean mixtures are completely oxidized.

2. Experimental

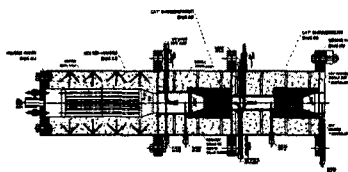
In Figure 2, the combustion system used in the experiments is shown. The experimental gas concentration and flow rates were controlled by mass flow meters. Only small amount of ammonia was added into the liquid natural gas (LNG) fuel line, and a large part of nitrogen was mixed with air in the combustion air line. As shown in Figure 3, the mixture of air and nitrogen was passing an electrically heated layer and was mixed again with fuels sprayed from a nozzle before being introduced to 1st honeycomb catalyst. The gases exiting from the 1st catalyst were

further mixed with the heated secondary air before entering the 2nd honeycomb catalyst. The sample gas was collected at the exit of catalyst beds respectively, and carried to the gas analyzers via sample line. The sampling and analysis system consisted of combustion gas analyzers (Horiba; FIA-510) for CO, O₂, CO₂ (Horiba; VIA-510) and unburned hydrocarbons (UHC), and NO_x analyzer (Thermo Environmental Instrument Inc.; 42H) for NO, NO₂ and NO_x. Also, CO, CH₄, H₂, NO, N₂O and NH₃ in the sample line were detected by a mass spectrometer (GeneSys). Concentration of gases measured by the mass spectrometer was relatively higher than that by the analyzers. Thus, the data between the analyzers and the mass spectrometer were adjusted with CO, CH₄ and NO for the consistency. In the experiment, hydrocarbon conversion was defined as a ratio of the converted hydrocarbon (difference between total inlet HC and UHC measured at the exit of the catalyst bed) to the total inlet HC concentration.

The catalytic metal components were supported on 400cpi cordierite honeycombs. Nitrate precursors were used for impregnation with the metal ions. For example, Pd(NO₃)₂ (Heesung Metal, 19.9% Pd) was impregnated onto La-doped Al₂O₃ (2 mol% La-Al₂O₃) supplied from Condea Inc. The surface area of La-doped Al₂O₃ was 90m²/g. The La-doped Al₂O₃ showed rather high thermal stability above 1000°C compared to the pure Al₂O₃. The activation procedure consisted of calcination in oxygen at 550°C for 6 h followed by reduction with hydrogen at 550°C for 4 h. For the mixed metal catalysts, monolith impregnated with Pd was subsequently impregnated with nitrate precursors for the second metals. Then, calcination and reduction were performed as above. The loading of the catalyst was expressed on a dry basis of washcoat materials, and the washcoat loading of the substrates. It is also noted that the 4%La-Al₂O₃ washcoat was calcined at 1000°C, whereas the 10%La-Al₂O₃ washcoat was calcined at 1200°C. The composition of catalysts used in the experiments is summarized in Table 1.



[Fig. 2] Schematic flow diagram of the apparatus used in the experiment



[Fig. 3] Two-step (fuel-rich and fuel-lean) catalytic burner

After the preparation, washcoat morphology and distribution of the catalyst metals were examined with SEM/EDX (Hitachi S-4700). As shown in Figure 4, the samples were not significantly different in the morphology of washcoat surface. However, it seems that 4%La-Al₂O₃ washcoat has more pores than 10%La-Al₂O₃, which is related to the BET surface area. In the EDX images, white spots exhibit catalyst metals. In general, catalyst metals were uniformly distributed on the washcoats. Also, high metal loadings show more white spots in the images.

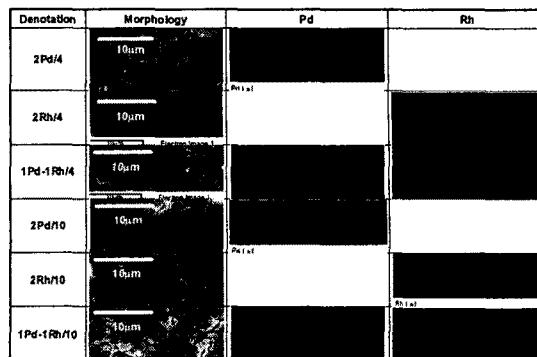
Table 1 The catalysts used in the experiments, sample name, precious metal/washcoat content.

| Denotation | Metal/Washcoat contents | Dimension | m ² /g |
|--------------------------|---|-----------|-------------------|
| 2Pd-10Ni/4 ^a | 2%Pd-10%NiO/4%La-Al ₂ O ₃ | Φ24 * L30 | n.m. ^c |
| 2Pd-10Ni/Nd ^b | 2%Pd-10%NiO/7%-10%Nd-Al ₂ O ₃ | Φ24 * L30 | n.m. ^c |
| 2Pd/4 ^a | 2%Pd/4%La-Al ₂ O ₃ | Φ24 * L30 | 26.95 |
| 1Pd-1Rh/4 ^a | 1%Pd-1%Rh/4%La-Al ₂ O ₃ | Φ24 * L30 | 37.12 |
| 1Pd-1Rh/10 ^b | 1%Pd-1%Rh/10%La-Al ₂ O ₃ | Φ24 * L30 | 22.80 |
| 2Rh/4 ^a | 2%Rh/4%La-Al ₂ O ₃ | Φ24 * L30 | 21.32 |
| 2Rh/10 ^b | 2%Rh/10%La-Al ₂ O ₃ | Φ24 * L30 | 26.88 |
| 2Pd/10 ^b | 2%Pd/10%La-Al ₂ O ₃ | Φ24 * L30 | 20.07 |
| 2Pt/4 ^a | 2%Pt/4%La-Al ₂ O ₃ | Φ24 * L10 | n.m. ^c |

a 4%La-Al₂O₃ washcoat was calcined at 1000°C.

b 10%La-Al₂O₃ washcoat was calcined at 1200°C.

c not measured

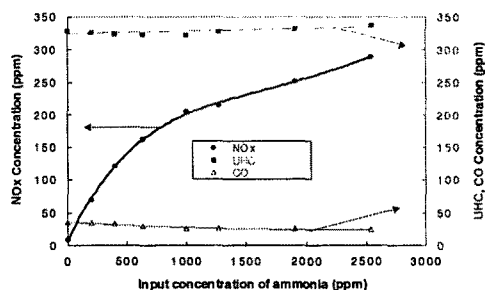


[Fig. 4] Morphology of washcoat surface and distribution of the catalyst metals.

3. Results and discussion

NH₃ conversion to NO in a turbulent diffusion flame:

A diffusion-type liquid propane (LP) nozzle burner (load capacity: ca. 2000kcal/hr) was temporarily mounted in place of the catalytic burner shown in Figure 2. Flame temperature of the LP module burner was controlled below 1300°C to minimize formation of thermal NO_x with increasing ammonia contents in the fuel. The obtained results are shown in Figure 5. The level of NH₃ conversion to NO is ca. 35% at low ammonia input (<1000ppm), and ca. 15% at high NH₃ concentrations (>1000ppm). High turndown (1/6-1/8) operations cause, in addition, a small amount of unburned HC and CO in flue gas.



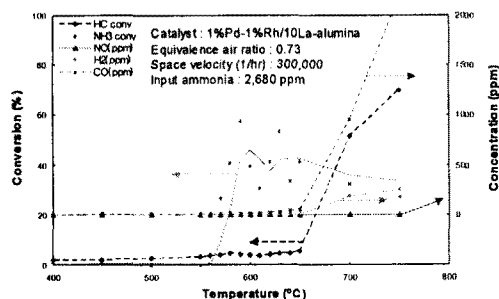
[Fig. 5] Ammonia conversion to NO in a turbulent diffusion flame under fuel-lean condition.

Effect of inlet temperature in the 1st catalyst:

Under fuel-rich conditions, the NO formation from NH₃ was extremely suppressed over the 1Pd-1Rh/10 catalyst even though the

concentration of CO and H₂ derived from methane was very low (see Figure 6). It was measured that the light-off temperature was 570°C for NH₃ and 650°C for CH₄. From the equations (2)–(5), it was shown that the hydrogen consumption to water vapor was more vigorous than the CO conversion to CO₂. Also, the equation (7) could be achieved in the presence of low H₂.

With increasing the inlet temperature, the decomposition of methane to CO and H₂ increased largely. However, the decomposition of methane little affected the NH₃ conversion to NO. It is worth noting that the NO₂ was not detected in this experiment, but a trace amount of the N₂O was observed at higher than 650°C.



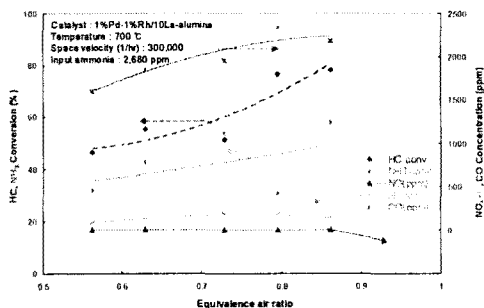
[Fig. 6] Effect of inlet temperature on NH₃ and HC conversion over the 1Pd-1Rh/10 catalyst under fuel-rich condition (equivalent air ratio ≈ 0.73) at a residence time of 0.012 second.

Effect of equivalent air ratio (Φ) in the 1st catalyst:

At far fuel-rich conditions, the NO formation was little affected by Φ , but it was a little sensitive by temperature rising accompanied with a slight increase of NH₃ consumption as shown in Figure 7. Methane conversion, on the other hand, was largely changed along Φ .

Over 1Pd-1Rh/10 catalyst, N₂O below 10 ppm is unexpectedly detected at 700°C in a range of $\Phi < 0.8$. On the other hand, in a range of $\Phi > 0.8$, N₂O is no more detected, but then the CO₂ more than 0.2% is observed. Despite of additional oxygen, reducing gases of CO and H₂ cause to constrain the NO formation and to accelerate the NH₃ conversion to N₂. However, the unreacted NH₃ at the 1st catalyst bed can be converted to the NO in

the 2nd catalytic layer under fuel-lean condition.



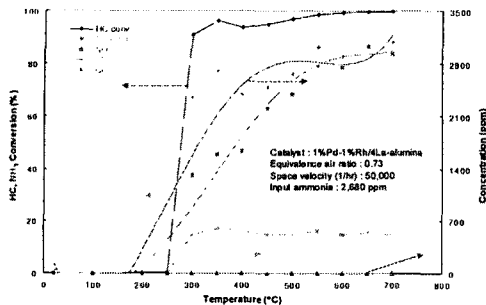
[Fig. 7] Effect of Φ on NH₃ and HC conversion over the 1Pd-1Rh/10 catalyst under fuel-rich condition ($0.56 < \Phi < 0.87$) at 700°C and a residence time of 0.012 second

Effect of space-velocity (SV) in the 1st catalyst:

As mentioned by Skreiberg et al. [5], in an isothermal reaction without catalyst, about 60% of NH₃ and 80% of NO were converted to the N₂ at 1000°C, in residence time of 1 second. It is required to find out a suitable residence time at low temperatures in our combustion system. To investigate a condition for enhancing conversion of NH₃ in high concentration of reductive gases, residence time in the 1st catalyst is changed from 0.012s to 0.072s by reducing the space velocity from 300,000/h to 50,000/h. The Figure 8 exhibits that the conversions of HC and NH₃ are respectively 98% and 85% at 550°C on 1Pd-1Rh/4 catalyst. Also, a trace amount of the NO is only detected at high temperatures, and a few NO₂ is observed at low temperatures.

In comparison with Figure 6, a large amount of H₂ and CO is generated above the light-off temperature defined as T₁₀ by HC concentration. It is worth noting that, in Figure 8, the light-off temperature seems to be appeared near 300°C, but the light-off temperature at the first measurement is actually observed at 430°C under the same reaction conditions. It appears as if the deviation of light-off point is contributed by the phenomena of hysteresis. It is also observed that the light-off temperature varies with space velocity. For example, the light-off temperatures at 50,000/h and 300,000/h of SV

are around 300°C (or 430°C) and 520°C respectively.



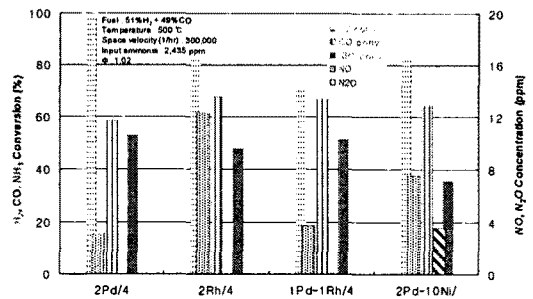
[Fig. 8] Effect of lower space velocity ($SV \approx 50,000$) on NH_3 and HC conversion over the 1Pd-1Rh/4 catalyst under fuel-rich condition ($\Phi \approx 0.73$) at a residence time of 0.072 second.

Comparison of catalytic activities among the 1st catalysts:

As the 1st catalyst should be able to convert NH_3 rather than the mixed gas of H_2 and CO with low generation of NO, the catalytic activity tests for fuel- NO_x formation from NH_3 in the presence of reductive gases were examined with a mixed fuel of 51% H_2 and 49% CO and with a small amount of NH_3 . At the state of $\Phi \approx 1.02$, Figure 9 shows that the test catalysts excellently convert NH_3 to N_2 rather than NO, where the conversion to NO is considerably less than 5% at 500°C. However, the unreacted NH_3 is still more than 40% of the inlet NH_3 at the condition of $\Phi \approx 1.02$ and $T \approx 500^\circ C$. The 1Pd-1Rh/4 catalyst seems to be superior in both conversions of NH_3 and the mixed gas of H_2 and CO. On the contrary, the 2Rh/4 catalyst is somewhat inferior in conversion of NH_3 , as NO formation is relatively high. It is suspected that the catalytic activity of 2Rh/4 in complete oxidation of CO and H_2 could affect NO generation. The inferior catalyst is also confirmed to have smaller BET surface area ($< 22m^2/g$) than the others ($> 25m^2/g$). 2Pd-10Ni/ catalyst also shows high NO formation and, exceptionally, N_2O below 10ppm is continuously detected at temperatures between 220°C and 700°C.

Near the stoichiometric point, both the steam reforming reaction [eq. (2)] and the direct oxidation reactions [eq. (4) & (5)] seem to be

simultaneously occurred in the presence of precious metal catalysts. It should be also noted that a flash-back of flame combustion is observed above 530°C for the mixed gas (the linear velocity of fluid was 0.8m/s at room temperature).



[Fig. 9] Comparison of catalytic conversion of NH_3 to NO near the stoichiometric point ($\Phi \approx 1.02$) at 500°C and a residence time of 0.012 second ($SV \approx 300,000$; inlet $y_{NH_3} \approx 2,435$ ppm).

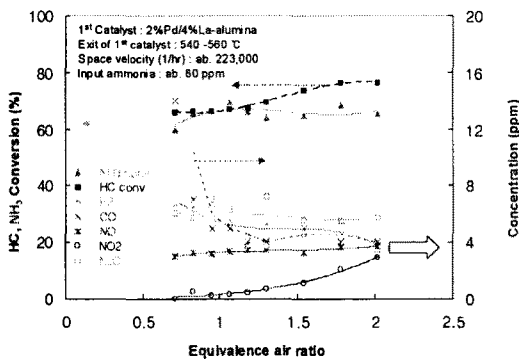
Fuel-lean catalytic reaction over the 2nd catalyst:

The facility has some limitations in control of temperature and flowrate for the 2nd fuel-lean catalytic combustion. The secondary air for the 2nd catalytic combustion was constantly supplied in a range of 540 ~ 565°C and the flowrate of the secondary air was adjusted to obtain ca. 0.8 of Φ at the inlet of the 2nd catalyst.

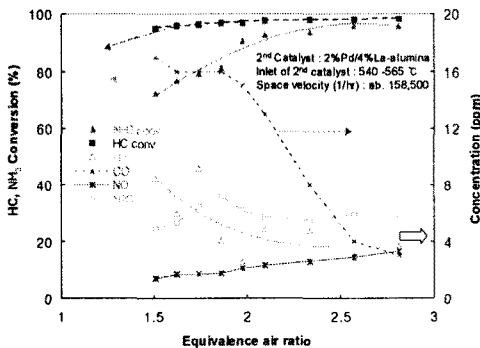
It is necessary to maintain high temperature at the exit of the 1st catalyst in order to achieve high conversion of NH_3 and HC, and to lower the pollutants of NO_x , N_2O and CO at the exit of the 2nd catalyst. The performance of the 2nd catalyst is deeply dependant on the results of the 1st catalyst in the test facility.

Figure 10 indicates that the conversion of NH_3 and HC is present in a range of 60 ~ 76% in the 1st catalyst, and 72 ~ 98% in the 2nd catalyst. As NO concentration is low in the 1st catalyst compared with the amount of the converted NH_3 , it is supposed that NO generated in the 1st catalyst could be converted to N_2 to a certain degree. In the 2nd catalyst, it is considered that most NO generated in the 1st catalyst can be reduced by H_2 and CO, and also it is possible that a

very small amount of NO is generated from the NH_3 conversion in the 2nd catalyst. On the other hand, it is observed that a small amount of CO and N_2O remains at the exit of the 2nd catalyst, which may result from low temperature of the secondary air. The conversion of NH_3 and HC is supposed to be highly affected by the residence time above 550°C in the 2nd catalyst, while the elimination of NO_x , N_2O and CO is rather dependant on the temperature.



(a)



(b)

[Fig. 10] A test result of two-step catalytic combustion with LNG-fuel bearing ammonia (a) at the exit of 1st catalyst (b) at the exit of 2nd catalyst.

4. Conclusion

The low content of NH_3 in CH_4 fuel bearing NH_3 contribute to convert to fuel- NO_x up to ca. 35% of the input in a diffusion flame. Under fuel-rich conditions, catalytic combustion technologies are more effective to control

simultaneously the NO generation and HC conversion from the fuel. Single precious metal or its bimetal catalysts maintain higher activities for HC conversion and at the same time high selectivity of NH_3 conversion to N_2 . By controlling equivalent air ratio, space velocity, inlet temperature, and catalyst component, the hydrocarbon conversion efficiency and the NH_3 conversion to N_2 can be achieved to be higher than 95%, while keeping the formation of NO below 5% of the inlet NH_3 . The unburned combustible gases of the fuel-rich combustion step are completely oxidized in the 2nd fuel-lean combustion step with reducing NO concentration.

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