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Characteristics of a stepwise fuel-rich/lean catalytic combustion of natural gas bearing ammonia

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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, 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.

Keywords: Stepwise catalytic combustion; Natural gas; Ammonia; Fuel-NO_x

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 N_2 by limiting the availability of oxygen during oxidation of the light volatiles containing NH_3 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. 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.

When burning biomass in a fluidized bed or on a grate in a reducing environment, initial conversion of the volatiles of biomass occurs at moderate temperatures. Glarborg et al. [6] proposed the pathways for formation of N_2 and NO from inlet NH_3 at moderate temperatures and under fuel-rich conditions. Brink et al. [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 NH_3. 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 N_2 was largely determined by the competition between reactions of N atoms with OH/O_2 (to form NO) and with NO (to form N_2). With the two proposed mechanisms of selective NH_3 conversion at fuel-lean conditions [5] and fuel-rich states [8], it can be deduced that the ammonia conversion to N_2 may occur in the presence of NO, and more effectively in the presence of reductive gases.

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Amblard et al. [9] reported that Ni catalyst supported on Al_2O_3 was effective for the selective conversion of NH_3 to N_2 in the presence of excess O_2. Nevertheless, in the same article it was also reported that Mn/Al_2O_3 and Fe/Al_2O_3 were more active than Ni/Al_2O_3, possibly because of the enhanced redox properties.

Kušar 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 $LaMnAl_{11}O_{19}$ enhanced the catalytic activity for methane in gasified waste. Substituting Mn into the crystal lattice of the spinel also increased the catalytic activity for H_2 and CO, while the methane activity remained low. The metal oxide catalysts also showed a higher selectivity for conversion of NH_3 into N_2 than the catalysts containing precious metals. The $Pd/LaMnAl_{11}O_{19}$ catalyst showed the highest activity for combustion of the synthetic gasified waste; H_2 ignited first, immediately followed by CO at 200 °C. Generally the oxidation of NH_3 followed CO and H_2 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 and 700 °C, ammonia conversion of the order 35–40% was obtained with low CO/H_2 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]:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O, \qquad \Delta H = -191.8\,\text{kcal/mol} \tag{1}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2, \qquad \Delta H = +49.2\,\text{kcal/mol} \tag{2}$$

$$CO + H_2O \rightarrow CO_2 + H_2, \qquad \Delta H = -9.8\,\text{kcal/mol} \tag{3}$$

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2, \qquad \Delta H = -8.5\,\text{kcal/mol} \tag{4}$$

$$CH_4 + 3/2O_2 \rightarrow CO + 2H_2O, \qquad \Delta H = -124.1\,\text{kcal/mol} \tag{5}$$

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

Following Eqs. (6)–(8) describe possible conversion of NH_3 and NO in a mixture of CO, H_2, NH_3, NO, and N_2 [11]. According to some reports [5,14], the reaction time in the isothermal region is considerable, ranging from more than 4 s at the lowest temperature of 430 °C to about 1 s 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.

$$2NH_3 + (5/2)O_2 \rightarrow 2NO + 3H_2O \tag{6}$$

$$2NO + CO \xrightarrow[\text{low}H_2]{} N_2 + CO_2 \tag{7}$$

$$NO + (5/2)H_2 \xrightarrow[\text{high}\,H_2]{} NH_3 + H_2O \tag{8}$$

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 first 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 second catalyst, NO generated in the first catalyst is reduced by the reductive gases decomposed from methane in the first catalyst (see Eq. (7)). At the same time, the remaining reductive gases including methane fuel-lean mixtures are completely oxidized.

2. Experimental

The catalytic metal components were supported on 400 cpi cordierite honeycombs. Nitrate precursors were used for impregnation with the metal ions. For example, $Pd(NO_3)_2$ (Heesung Metal, 19.9% Pd) was impregnated onto La-doped Al_2O_3 (2 mol% La-Al_2O_3) supplied from Condea Inc. The surface area of La-doped Al_2O_3 was 90 m^2/g. The La-doped Al_2O_3 showed rather high thermal stability above 1000 °C compared to the pure Al_2O_3. 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-Al_2O_3 washcoat was calcined at 1000 °C, whereas the 10% La-Al_2O_3 washcoat was calcined at 1200 °C. The composition of catalysts used in the experiments is summarized in Table 1.

After the preparation, washcoat morphology and distribution of the catalyst metals were examined with SEM/EDX (Hitachi S-4700). As shown in Fig. 1, the samples were not significantly different in the morphology of washcoat surface. However, it seems that 4% La-Al_2O_3 washcoat has more pores than 10% La-Al_2O_3, 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.

The combustion test system used in the experiments was shown in Fig. 2. The liquid natural gas (LNG) fuel and mixed fuel of carbon monoxide (CO) and hydrogen (H_2) were

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

Denotation	Metal/washcoat contents	Dimension (mm)	BET surface area (m^2/g)
2Pd–10Ni/4[a]	2% Pd–10% NiO/4% La-Al_2O_3	Ø24 × L30	n.m.[c]
2Pd–10Ni/Nd[b]	2% Pd–10% NiO/7–10% Nd-Al_2O_3	Ø24 × L30	n.m.[c]
2Pd/4[a]	2% Pd/4% La-Al_2O_3	Ø24 × L30	26.95
1Pd–1Rh/4[a]	1% Pd–1% Rh/4% La-Al_2O_3	Ø24 × L30	37.12
1Pd–1Rh/10[b]	1% Pd–1% Rh/10% La-Al_2O_3	Ø24 × L30	22.80
2Rh/4[a]	2% Rh/4% La-Al_2O_3	Ø24 × L30	21.32
2Rh/10[b]	2% Rh/10% La-Al_2O_3	Ø24 × L30	26.88
2Pd/10[b]	2% Pd/10% La-Al_2O_3	Ø24 × L30	20.07
2Pt/4[a]	2% Pt/4% La-Al_2O_3	Ø24 × L10	n.m.[c]

[a] Four percent La-Al_2O_3 washcoat was calcined at 1000 °C.
[b] Ten percent La-Al_2O_3 washcoat was calcined at 1200 °C.
[c] Not measured.

controlled by mass flow meters. Only small amount of ammonia was added into the fuel line, and a large part of nitrogen was mixed with air in the combustion air line. As shown in Fig. 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 the first honeycomb catalyst. The gases exiting from the first catalyst were further mixed with the heated secondary air before entering the second honeycomb catalyst. The sample gas was collected at the exits of the first and the second catalyst beds, respectively, and carried to the gas analyzers via a sample line. The sampling and analysis system consisted of combustion gas analyzers (Horiba; FIA-510) for CO, O_2, CO_2 (Horiba; VIA-510) and unburned hydrocarbons (UHC), and NO_x analyzer (Thermo Environmental Instrument Inc.; 42H) for NO, NO_2 and NO_x. Also, CO, CH_4, H_2, NO, N_2O and NH_3 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, CH_4 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.

3. Results and discussion

3.1. NH_3 conversion to NO in a turbulent diffusion flame

A diffusion-type liquid propane (LP) nozzle burner (load capacity: ca. 2000 kcal/h) was temporarily mounted in place of the catalytic burner shown in Fig. 3. 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

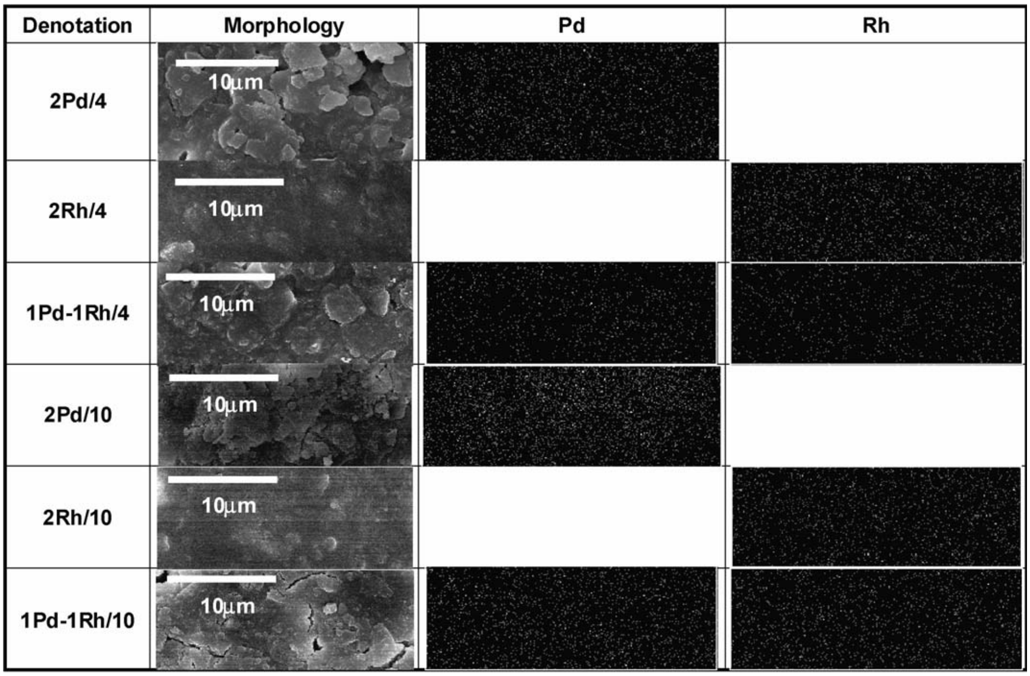

Fig. 1. Morphology of washcoat surface and distribution of the catalyst metals.

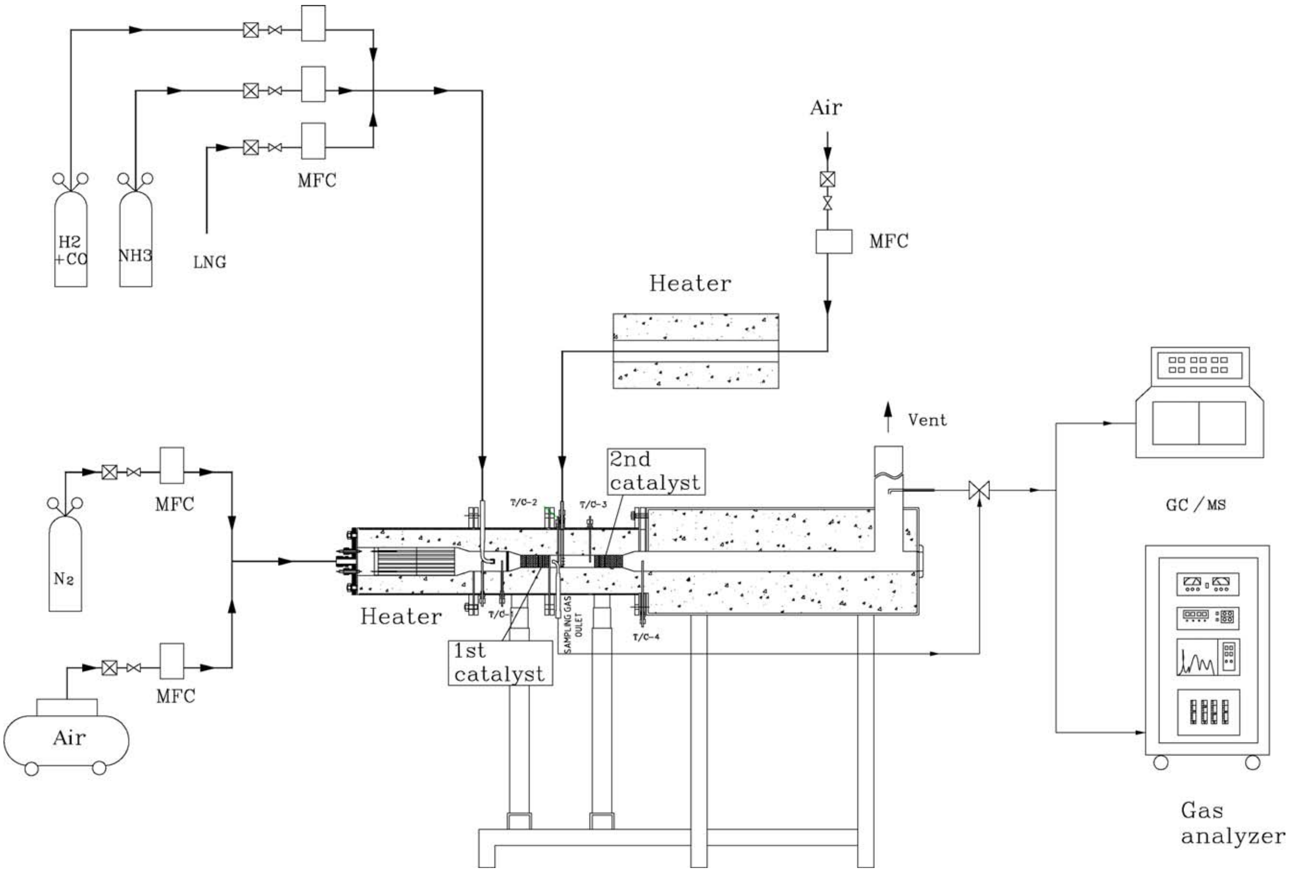

Fig. 2. Schematic flow diagram of the apparatus used in the experiments.

shown in Fig. 4. The level of NH_3 conversion to NO is ca. 35% at low ammonia input (<1000 ppm), and ca. 15% at high NH_3 concentrations (>1000 ppm). High turndown (1/6–1/8) operations cause, in addition, a small amount of unburned HC and CO in flue gas.

3.2. Effect of inlet temperature in the first catalyst

Under fuel-rich conditions, the NO formation from NH_3 was extremely suppressed over the 1Pd–1Rh/10 catalyst even though the concentration of CO and H_2 derived from methane

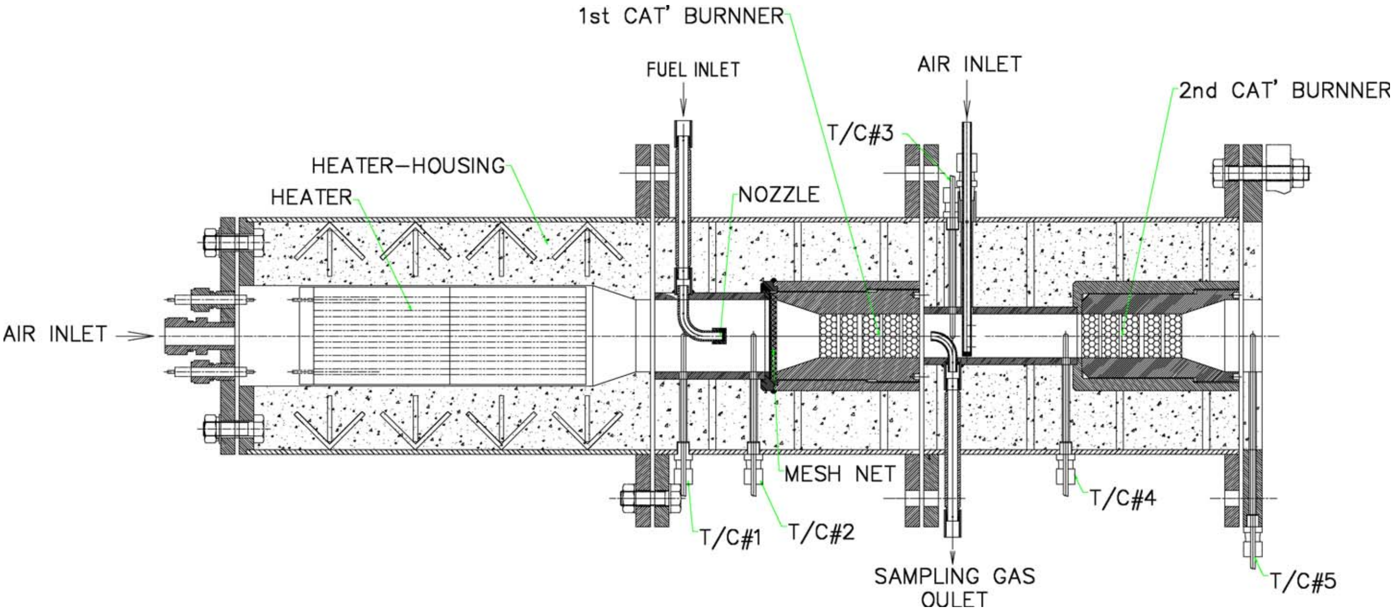

Fig. 3. Two-step (fuel-rich and fuel-lean) catalytic burner.

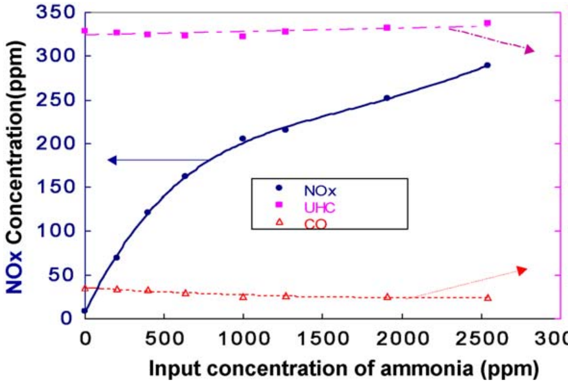

Fig. 4. Ammonia conversion to NO in a turbulent diffusion flame under fuel-lean condition.

was very low (see Fig. 5). It was measured that the light-off temperature was 570 °C for NH_3 and 650 °C for CH_4. From Eqs. (2)–(5), it was shown that the hydrogen consumption to water vapor was more vigorous than the CO conversion to CO_2. Also, Eq. (7) could be achieved in the presence of low H_2.

With increasing the inlet temperature, the decomposition of methane to CO and H_2 increased largely. However, the decomposition of methane little affected the NH_3 conversion to NO. It is worth noting that the NO_2 was not detected in this experiment, but a trace amount of the N_2O was observed at higher than 650 °C.

3.3. Effect of equivalent air ratio (Φ) in the first 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 NH_3 consumption (see Fig. 6). Methane conversion, on the other hand, was largely changed along Φ.

Over 1Pd–1Rh/10 catalyst, N_2O below 10 ppm is unexpectedly detected at 700 °C in a range of $\Phi < 0.8$. On the other hand, in a range of $\Phi > 0.8$, N_2O is no more detected, but then the CO_2 more than 0.2% is observed. Despite of additional oxygen, reducing gases of CO and H_2 cause to constrain the NO formation and to accelerate the NH_3 conversion to N_2. However, the unreacted NH_3 at the first catalyst bed can be converted to the NO in the second catalytic layer under fuel-lean condition.

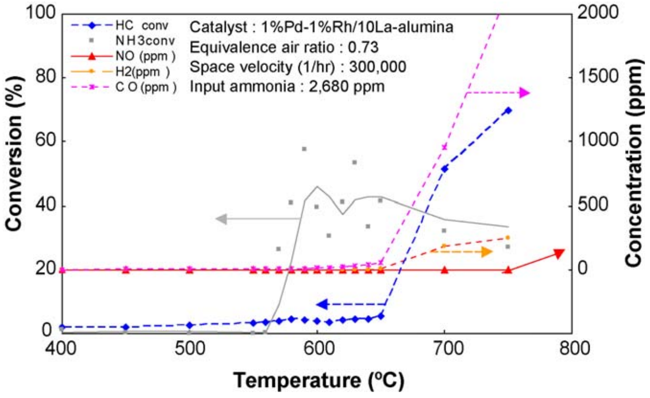

Fig. 5. Effect of inlet temperature on NH_3 and HC conversion over the 1Pd–1Rh/10 catalyst under fuel-rich condition (equivalent air ratio ≈ 0.73) at a residence time of 0.012 s.

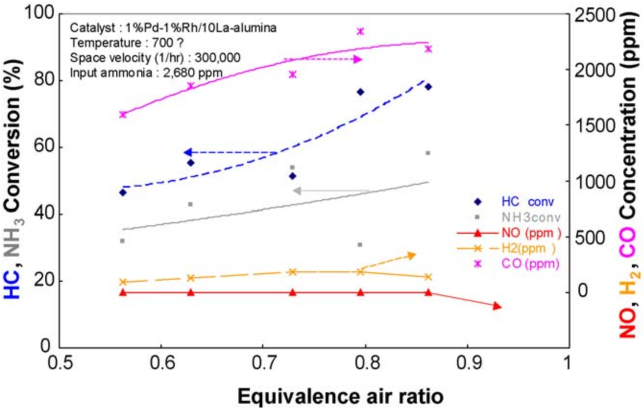

Fig. 6. Effect of Φ on NH_3 and HC conversion over the 1Pd–1Rh/10 catalyst under fuel-rich condition ($0.56 < \Phi < 0.87$) at 700 °C and a residence time of 0.012 s.

3.4. Effect of space velocity (SV) in the first catalyst

As mentioned by Skreiberg et al. [8], in an isothermal reaction without catalyst, about 60% of NH_3 and 80% of NO were converted to the N_2 at 1000 °C, in residence time of 1 s. 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 NH_3 in high concentration of reductive gases, residence time in the first catalyst is changed from 0.012 to 0.072 s by reducing the space velocity from 300,000 to 50,000 h^{-1}. Fig. 7 exhibits that the conversions of HC and NH_3 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 NO_2 is observed at low temperatures.

In comparison with Fig. 5, a large amount of H_2 and CO is generated above the light-off temperature defined as T_{10} by HC concentration. It is worth noting that, in Fig. 7, the light-off temperature seems to be appeared near 300 °C, but the light-off temperature at the first measurement is actually observed at

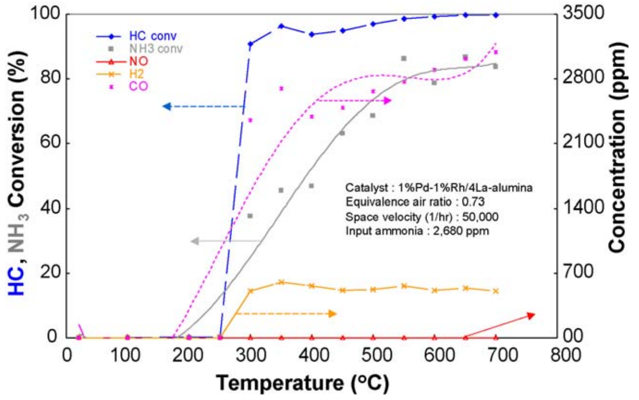

Fig. 7. Effect of lower space velocity (SV ≈ 50,000) on NH_3 and HC conversion over the 1Pd–1Rh/4 catalyst under fuel-rich condition ($\Phi \approx 0.73$) at a residence time of 0.072 s.

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 and 300,000 h^{-1} of SV are around 300 (or 430 °C) and 520 °C, respectively.

3.5. Comparison of catalytic activities among the first catalysts

As the first 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 $\Phi \approx 1.02$, Fig. 8 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 $T \approx 500$ °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 (<22 m^2/g) than the others (>25 m^2/g). 2Pd–10Ni/ catalyst also shows high NO formation and, exceptionally, N_2O below 10 ppm is continuously detected at temperatures between 220 and 700 °C.

Near the stoichiometric point, both the steam reforming reaction (Eq. (2)) and the direct oxidation reactions (Eqs. (4) and (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 0.8 m/s at room temperature).

3.6. Fuel-lean catalytic reaction over the second catalyst

The two-step catalytic combustion test was conducted in the experimental facility as shown in Fig. 3. The facility has some limitations in control of temperature and flowrate for the second fuel-lean catalytic combustion. The secondary air for the second 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 second catalyst.

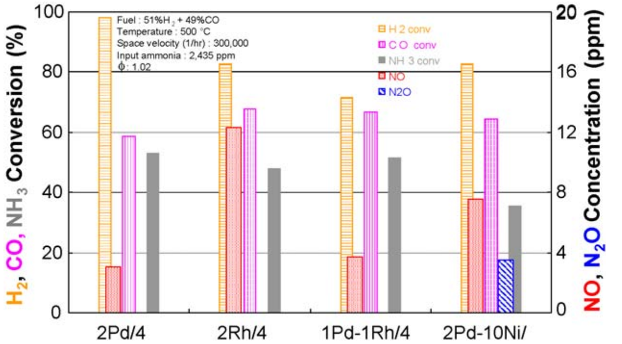

Fig. 8. Comparison of catalytic conversion of NH_3 to NO near the stoichiometric point ($\Phi \approx 1.02$) at 500 °C and a residence time of 0.012 s (SV ≈ 300,000; inlet $y_{NH_3} \cong 2435$ ppm).

It is necessary to maintain high temperature at the exit of the first 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 second catalyst. The performance of the second catalyst is deeply dependant on the results of the first catalyst in the test facility.

Fig. 9 indicates that the conversion of NH_3 and HC is present in a range of 60–76% in the first catalyst, and 72–98% in the second catalyst. As NO concentration is low in the first catalyst compared with the amount of the converted NH_3, it is supposed that NO generated in the first catalyst could be converted to N_2 to a certain degree. In the second catalyst, it is considered that most NO generated in the first 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 second catalyst. On the other hand, it is observed that a small amount of CO and N_2O remains at the exit of the second 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 second catalyst, while the elimination of NO_x, N_2O and CO is rather dependant on the temperature.

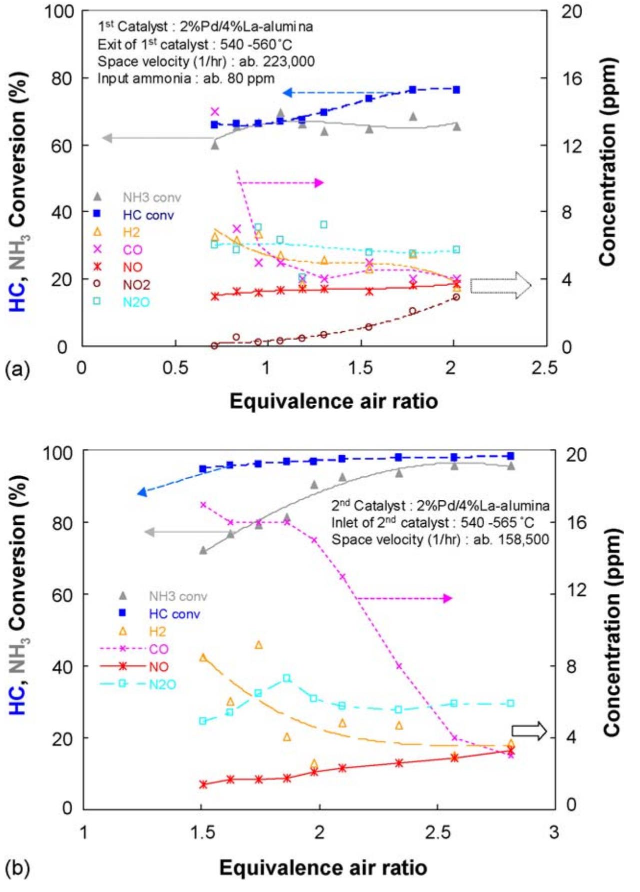

Fig. 9. A test result of two-step catalytic combustion with LNG-fuel bearing ammonia (a) at the exit of the first catalyst (b) at the exit of the second catalyst.

4. Conclusions

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 second fuel-lean combustion step with reducing NO concentration.

Acknowledgements

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