A NOVEL CATALYTIC METHANE DE-NO\textsubscript{X} SYSTEM FOR SMALL GHP AND CHP

Hirofumi Ohtsuka, Osaka Gas Co., Ltd., Osaka, Japan
Kenji Baba, Osaka Gas Co., Ltd., Osaka, Japan
Takayuki Inoue, Osaka Gas Co., Ltd., Osaka, Japan

1. INTRODUCTION

There is still a need for a convenient de-NO\textsubscript{x} system which can be applied to small gas engine-driven heat pumps (GHP) and combined heat and power (CHP) plants. The selective catalytic reduction of NO\textsubscript{x} by ammonia (ammonia-SCR) has been successfully applied to large CHPs since the early ‘90s when the urea-SCR system, which uses a urea solution instead of hazardous NH\textsubscript{3} cylinder or concentrated NH\textsubscript{3} solution, was developed. However, there are still problems which prevent its application to smaller systems: (i) possible ammonia leak when an excess amount of urea solution is added, (ii) difficulties in supplying urea solution.

Intensive research has been devoted to the selective catalytic reduction by hydrocarbons, mainly by the automobile and auto-catalyst industries. If the fuel as is can be used as the reductant, there is no need to supply chemicals such as urea for the reductant. Moreover, any unreacted reductant can be removed by oxidation catalysts with no production of further pollutants. However, its performance and durability are still insufficient for practical applications, and its application is still limited to specific cases.

To apply the selective catalytic reduction by hydrocarbons to natural gas-fired GHP or CHP, methane must be used as the reductant. To date, various catalysts such as Co ion-exchanged zeolites [1,2], In or Ga ion-exchanged zeolites [3,4], and Pd ion-exchanged zeolites [5,6] have been reported as catalysts for the selective reduction of NO\textsubscript{x} by methane. However, most of these catalysts lose activity in the presence of water vapor [7]. Only Pd-based catalysts show an activity of a practically applicable level even in the presence of water vapor [8]. However, the durability of Pd-based catalysts is not sufficient for practical applications.

In this report, we show that a novel catalyst, Pd-Pt/Fe-doped sulfated zirconia, has sufficient durability for the selective reduction of NO\textsubscript{x} by methane under the actual reaction conditions of the exhaust from gas engine-driven GHP and CHPs.

2. EXPERIMENTAL

2.1. Catalyst Preparation

Sulfated zirconia (SZ) was prepared by immersing zirconium hydroxide (Mitsuwa Chemical,
Osaka) in an aqueous solution of ammonium sulfate (Hayashi Pure Chemicals, Osaka). Water was removed in a rotary evaporator. The solid was dried and calcined in air at 550°C. XRD analysis revealed that the SZ mostly consisted of the tetragonal phase. Iron-doped SZ was prepared in a similar manner except that iron (II) sulfate and a small amount of sulfuric acid were added to the solution. Sulfuric acid was added to avoid the precipitation of iron (III) hydroxide when iron (II) cations were oxidized by atmospheric oxygen. Palladium and platinum were loaded by impregnation using aqueous solutions prepared from Pd(NO$_3$)$_2$ and Pt(NH$_3$)$_4$(NO$_3$)$_2$ (N. E. Chemcat, Tokyo). The impregnated solid was dried and calcined in air at 500°C.

Zeolite catalysts were prepared by the usual ion exchange method. H-form Mordenite (SiO$_2$/Al$_2$O$_3$ ratio 16, Tosoh Corp., Shin-nan-yo, Japan) was suspended in a solution of Pd(NH$_3$)$_4$(NO$_3$)$_2$ (N.E. Chemcat) and kept at 60°C for 15 h. After filtration, the solid was dried and calcined in air at 500°C. The amount of loaded Pd was analyzed by ICP spectrometry. In the preparation of Pd-Pt/MOR, a solution containing both Pd(NH$_3$)$_4$(NO$_3$)$_2$ and Pt(NH$_3$)$_4$(NO$_3$)$_2$ was used.

2.2. Activity Test

Catalytic activity tests were carried out using a fixed-bed flow reactor. The catalyst was pressed into pellets, crushed and sieved into 1-2 mm grains. The sieved catalyst (4 ml) was placed in a stainless steel reactor (i.d. 14 mm). The temperature of the catalyst bed was measured by thermocouples inserted into the reactor. Reaction gases were generated by mixing NO/He, CH$_4$/He, C$_2$H$_6$/He, C$_3$H$_8$/He, SO$_2$/He, O$_2$, and He gases in cylinders using mass flow controllers. Water was fed by a syringe pump (Furue Science, Tokyo) through a vaporizer kept at 300°C. The concentrations of NO and NO$_2$ were measured by a chemiluminescence NOx analyzer equipped with an NO$_2$ converter (Yanaco Analytical Systems, Kyoto). The concentrations of CH$_4$, C$_2$H$_6$, C$_3$H$_8$, CO, CO$_2$, N$_2$ and N$_2$O were measured by a gas chromatograph (Yanaco Analytical Systems).

2.3. Durability Test

Long-term durability tests were carried out using a fixed-bed flow reactor similar to the one used in the activity tests. The major differences were as follows: the reactor was made of quartz; the reaction gases were generated by mixing NO/N$_2$, CH$_4$/N$_2$, SO$_2$/N$_2$, O$_2$, CO$_2$ and N$_2$ gases.

3. RESULTS AND DISCUSSIONS

3.1. Comparison of Pd-Pt/Sulfated Zirconia and Pd/MOR

Figure 1 compares the activity of Pd/SZ, Pd-Pt/SZ, Pd/MOR, and Pd-Pt/MOR. Uchida et al. reported that Pd/MOR showed NOx conversions of ca.80% at 400°C under a condition simulating an exhaust from natural gas combustion. The result in Fig. 1 is in agreement with their results. A maximum NOx conversion of 30% was obtained at 450°C over Pd/SZ. The activity of Pd/SZ for the selective reduction of NOx by methane has already been reported by Loughran and Resasco [9]. Its
activity under practical conditions, however, is not sufficient. Adding Pt greatly improved NOx conversion. Sulfated zirconia loaded with Pd and Pt showed NOx conversions of ca. 50% at 400 – 450°C. The effect of Pt was pronounced at lower temperatures and was small at 500°C. A similar effect was also observed on Pd/MOR.

Figure 2 shows the change of NOx and methane conversions with time on stream over Pd-Pt/SZ. In the absence of SO2, a continuous decrease in NOx conversion was observed, while the conversion of methane became stable after 25 h. This means that the selectivity for NOx reduction decreased with time on stream. In the presence of 3-ppm SO2, however, the catalyst showed stable activity for NOx reduction. It kept a NOx conversion higher than 50% for more than 100 h.

Figure 3 shows the change of NOx and methane conversions with time on stream over Pd/MOR. In the absence of SO2, it initially showed a NOx conversion of ca. 70%. However, its NOx conversion continuously decreased with time. Hoshi et al. examined the effect of water vapor on the deactivation of Pd/MOR and showed that the durability was significantly affected by the presence of water vapor [10]. Their results showed that the catalyst maintained a NOx conversion of ca. 50% in the presence of 2% water vapor for 70 h, while it decreased from 50% to 10% in the presence of 9% water vapor. The result shown in Fig. 3 is in agreement with their results. The effect of SO2 on Pd/MOR was fatal. Its initial NOx conversion of ca. 60% was completely lost after 50 h on stream. Similar tests were carried out for Pd-Pt/MOR. The catalyst showed rapid deactivation both in the presence and absence of SO2. Its NOx conversions after 50 h on stream was 9 and 18% in the presence and absence of SO2, respectively. This indicates that the improved durability of Pd-Pt/SZ is not the direct result of Pt.

Water vapor and sulfur oxides are inevitable in the combustion exhaust of any fossil fuel. The concentration of water vapor in the combustion exhaust of natural gas varies with the excess air ratio \( \lambda \) and is usually within the range of 10-15 vol %. Sulfur oxides (SOx) are produced by the combustion of organic sulfur compounds. Most of the SOx is present as sulfur dioxide (SO2). Because city gas contains organic sulfur compounds as odorants, the SOx concentration in exhaust is usually at a sub-ppm level, even when liquefied natural gas, which is practically free from sulfur compounds, is used as the feedstock.

Among the various catalysts that have been reported to be active for the reaction, only Pd-based catalysts have been reported to have practical activity in the presence of water vapor. The result in Fig. 3 showed, however, that the catalyst is not durable under practical conditions. On the other hand, Pd-Pt/SZ showed stable activity even in the presence of water vapor and SOx. It is widely known that sulfur compounds cause severe catalyst poisoning. In the case of zeolite catalysts, physical poisoning by micropore blocking also causes a severe effect in addition to the poisoning caused by direct interaction with active sites [11]. Since SZ does not contain micropores, poisoning by micropore blocking does not occur on Pd-Pt/SZ. The stabilization of activity by SOx is probably caused by the stabilization of the surface sulfate. It is widely accepted that acid sites play key roles in NOx reduction on Pd-based catalysts [12, 13]. Since the acid site of SZ consist of sulfate, which
can be lost by desorption, feeding SOx can stabilize the acid sites by refilling the lost sulfate.

Fig. 1. Temperature dependence of the activity. Left: 0.5% Pd/SZ (open symbol), 0.38% Pd-0.12% Pt/SZ (filled symbol). Right: 0.42% Pd/MOR (open symbol), 0.38% Pd-0.27% Pt/MOR (filled symbol). Circle: NOx conversion. Triangle: CH₄ conversion. Reaction conditions: NO 150 ppm, CH₄ 2000 ppm, O₂ 10%, H₂O 9%, He balance, GHSV 15,000 h⁻¹.

Fig. 2. Change of NOx and CH₄ conversions with time over 0.38% Pd-0.12% Pt/SZ. Reaction conditions: NO 150 ppm, CH₄ 2000 ppm, O₂ 10%, H₂O 9%, SO₂ 0 or 3 ppm, He balance, 450°C, GHSV 15,000 h⁻¹. Circle: NOx conversion. Triangle: CH₄ conversion.

Fig. 3. Change of NOx and CH₄ conversions with time over 0.42% Pd/MOR. Reaction conditions and symbols: same as in Fig. 2.
3.2. Effect of Reductant and Reaction Conditions

Figure 4 shows the effect of the reductant. Conversions of NOx are compared under the same amount (2000 ppm) of reductant in the THC basis. The maximum NOx conversion of ca. 50% was obtained at 400 - 450°C by using methane. Only 35% was obtained when ethane was used, and only 23% when propane was used. As indicated by the hydrocarbon conversion, higher hydrocarbons have higher reactivity. Accordingly, the temperature of the maximum NOx conversion decreases. The change of the maximum conversion with the carbon number of the reductant suggests that the number of reduced NOx molecules per reductant molecule does not differ among these reductant species. Figure 4 also shows the hydrocarbon conversion in the absence of NOx, which is the activity of hydrocarbon combustion. The conversion curves shift to higher temperatures in the absence of NOx. In the temperature range between the two curves, hydrocarbons are activated only by NOx and not by oxygen. A high selectivity for NOx reduction is usually obtained in this temperature range [14]. This is also true on Pd-Pt/SZ regardless of the carbon number of the reductant, i.e., the maximum NOx conversion is obtained at the temperature where the difference in HC conversion in the presence and absence of NOx is at the maximum.

![Figure 4](image_url)

Fig. 4. The effect of reductant carbon number on the selective reduction of NOx over Pd-Pt/SZ. Reaction conditions: NO 0 (closed symbol) or 150 ppm (open symbol), HC 2000 ppm as C, O₂ 10%, H₂O 9%, He balance, GHSV 15,000 h⁻¹. Hydrocarbon: methane (circle), ethane (diamond), propane (star).

Figure 5 shows the effect of water vapor. In the absence of water vapor, a maximum NOx conversion of ca. 80% was obtained between 400-450°C. The NOx conversion is higher than that obtained in the absence of water vapor. However, in the absence of water, a significant amount of N₂O was observed in the effluent gas. Nitrous oxide is considered to be harmless in terms of the local environment because it does not cause acid rain or photochemical smog. However, it has a strong greenhouse effect. Therefore, emissions of nitrous oxide should be minimized. The
formation of N$_2$O in the selective reduction of NOx by hydrocarbons over Pt-based catalysts has been reported by several research groups [15, 16] and is considered to be a major problem of Pt-based catalysts. However, N$_2$O formation was not observed in the presence of water vapor. The reason for the suppression of N$_2$O formation by water is not clear at present.

![Graph showing the effect of water vapor on the selective reduction of NOx by methane and methane oxidation over 0.38% Pd-0.12% Pt/SZ. Reaction conditions: NO 0 or 500 ppm, CH$_4$ 2000 ppm, O$_2$ 10%, H$_2$O 0 (right) or 9% (left), He balance, 450ºC, GHSV 15,000 h$^{-1}$. NO-CH$_4$-O$_2$: NOx conversion (circle), CH$_4$ conversion (triangle), NOx conversion to N$_2$O (half-filled circle). CH$_4$-O$_2$: CH$_4$ conversion (inverted triangle).](image)

**Fig. 5.** The effect of water vapor on the selective reduction of NOx by methane and methane oxidation over 0.38% Pd-0.12% Pt/SZ. Reaction conditions: NO 0 or 500 ppm, CH$_4$ 2000 ppm, O$_2$ 10%, H$_2$O 0 (right) or 9% (left), He balance, 450ºC, GHSV 15,000 h$^{-1}$. NO-CH$_4$-O$_2$: NOx conversion (circle), CH$_4$ conversion (triangle), NOx conversion to N$_2$O (half-filled circle). CH$_4$-O$_2$: CH$_4$ conversion (inverted triangle).

### 3.3. Effect of Iron Addition on the Long-term Durability

For practical applications in exhaust treatment, the catalyst should be durable for more than several thousand hours. The durability of the catalyst was examined under conditions simulating an exhaust from lean-burn gas engines. The results are shown in Figs. 6 and 7. Pd-Pt/SZ showed a gradual decrease in both NOx and methane conversions at 450ºC. On the other hand, Pd-Pt/Fe-promoted SZ showed a gradual increase in NOx conversion in the initial 20 h and maintained a NOx conversion of ca. 60% for 700 h at 450ºC. At 500ºC, deactivation of Pd-Pt/SZ was more rapid. It showed a maximum NOx conversion of 50% after 3 h on stream, but the conversion fell to 20% after 300 h. On the other hand, its methane conversion remained around 90%, which means that the selectivity for NO reduction decreased. Surprisingly, Pd-Pt/Fe-promoted SZ showed a stable NOx conversion higher than 70% for over 2400 h. The conversion was higher than the maximum conversion obtained over Pd-Pt/SZ (Fig. 1). A similar test was carried out at 525ºC. The NOx conversion over Pd-Pt/Fe-SZ after 1200 h on stream was 63% and was stable. A comparison of methane conversions indicates the suppression of methane conversion by Fe. Over Pd-Pt/SZ, NOx conversion reaches a maximum at 450ºC. This is because methane combustion, a competing reaction, consumes the reductant, as shown in Fig. 4. The fact that Pd-Pt/Fe-promoted SZ showed higher NOx conversion at 500ºC than at 450ºC suggests that the suppression of methane combustion caused the improved selectivity for NOx reduction. The promotion of the alkane isomerization reaction over SZ by adding Fe is widely known. It is proposed that Fe-SZ has stronger acidity than
Because acid sites are indispensable for the reaction, the stronger acidity of Fe-SZ may also cause the improvement in NOx reduction.

Figure 8 shows the dependency of the NOx conversion on the NOx and methane concentration over Pd-Pt/Fe-promoted SZ. Because the catalyst shows an induction period of activity, the catalyst was treated with the reaction mixture for 30 h at 500°C before the measurement. The NOx conversion slightly decreased when the methane concentration decreased from 2000 ppm to 1000 ppm. The dependency of NOx conversion on NOx concentration was observed at 450°C, but was small at 500°C.

Fig. 6. Durability of Pd-Pt/SZ (left) and Pd-Pt/Fe-promoted SZ (right). Reaction conditions: NO 150 ppm, CH₄ 2000 ppm, O₂ 10%, CO₂ 6%, H₂O 9%, SO₂ 0.3 ppm, N₂ balance, 450°C, GHSV 15,000 h⁻¹. Circle: NOx conversion. Triangle: CH₄ conversion.

Fig. 7. Durability of Pd-Pt/SZ (left) and Pd-Pt/Fe-promoted SZ (right). Reaction conditions: NO 150 ppm, CH₄ 2000 ppm, O₂ 10%, CO₂ 6%, H₂O 9%, SO₂ 0.3 ppm, N₂ balance, 500°C, GHSV 15,000 h⁻¹. Symbols: same as in Fig. 6.
4. CONCLUSIONS

Durability tests under conditions of lean-burn gas engine exhaust showed that Fe-doped sulfated zirconia loaded with Pd and Pt has sufficient activity and durability for NOx reduction by methane in the presence of excess oxygen (10 vol.%), water vapor (9 vol.%) and sulfur dioxide (0.3 vol. ppm).

Within the temperature range of 450 to 525ºC, a NOx conversion higher than 60% can be obtained at a GHSV of 15,000 h⁻¹, which is comparable with the typical catalyst volume of ammonia-SCR.

REFERENCES


