1. Introduction

Three-way catalysts (TWCs) can efficiently remove harmful components, such as carbon monoxide (CO), hydrocarbons (HCs) and nitrogen oxides (NOx), emitted from gasoline engines via catalytic reactions which simultaneously achieve oxidation of CO and HCs and reduction of NOx\(^1\),\(^2\). However, these three-way catalytic reactions are very complicated because of the several reaction pathways such as water-gas-shift, steam-reforming and others\(^6\). Three-way catalytic reactions are also known to be affected by the support materials for platinum group metals (PGMs)\(^7\)\(^\text{–}\)\(^{11}\). For example, alumina is often used as a support for Rh because of its high thermal stability and high specific surface area\(^1\)\(^2\)\(^\text{–}\)\(^6\). However, these three-way catalytic reactions are very complicated because of the several reaction pathways such as water-gas-shift, steam-reforming and others\(^2\)\(^\text{–}\)\(^6\). Three-way catalytic reactions are also known to be affected by the support materials for platinum group metals (PGMs)\(^7\)\(^\text{–}\)\(^{11}\). For example, alumina is often used as a support for Rh because of its high thermal stability and high specific surface area\(^1\)\(^2\)\(^\text{–}\)\(^6\). CeO\(_2\)-ZrO\(_2\) (CZ) is also common as an essential component because the oxygen concentration on the catalyst surface can be adjusted by reversibly changing the valence of the Ce cation between Ce\(^{4+}\) and Ce\(^{3+}\) to achieve the so-called "oxygen storage capacity (OSC)"\(^1\)\(^2\)\(^\text{–}\)\(^{10}\) under actual exhaust gas conditions, where the contents of the exhaust gas fluctuate depending on the air-to-fuel ratio\(^1\)\(^2\). Therefore, the development of suitable combinations of support materials is important to achieve high performance.

We have recently investigated the activity of Rh catalysts using alumina (Rh/Al) and CZ (Rh/CZ) as support materials, and found that Rh supported on alumina showed higher light-off performance than Rh supported on CZ\(^1\)\(^5\). However, NO conversion on Rh/Al no longer increased above the temperature at which NO conversion was achieved at 80 % (\(T_{80}\)), whereas NO conversion gradually decreased over Rh/CZ under lean/rich perturbation conditions. Catalytic performance for TWC reactions in higher temperature regions is well known to depend on the OSC properties of TWC\(^1\)\(^6\),\(^1\)\(^7\). We also found that a mixture of Rh/Al and CZ (Rh/Al\(^\text{–}\)CZ) showed higher NO conversion than only Rh/Al in higher and lower temperature regions\(^1\)\(^5\). Temperature-programmed reduction by H\(_2\) (H\(_2\)-TPR) identified novel Rh-CZ interactions in Rh/Al\(^\text{–}\)CZ catalyst, although Rh was not directly deposited Rh on CZ during sample preparation. More prominent activity was observed for the combination of Rh/Al and CZ aged in air at 1000 °C. Migration of Rh from alumina to CZ during high-temperature ageing in air was suspected, resulting in the novel Rh-CZ interactions.

The three-way catalytic reactions are greatly influenced by the state of the PGMs\(^1\)\(^8\),\(^\text{–}\)\(^2\)\(^1\). In particular, the catalytic performance of Rh deteriorates depending...
Rhodium catalyst supported on alumina (Rh/Al) was first prepared by incipient wetness impregnation of commercial γ-alumina (La stabilized Al₂O₃, BET surface area: 140 m² g⁻¹) with an aqueous solution of Rh(NO₃)₃, followed by drying at 120 °C for 12 h, and calcining at 550 °C for 30 min in air. The loading of Rh was fixed at 2.0 wt%. Rh/Al + CZ was obtained by mixing 2.0 wt% Rh/Al with commercial CeO₂-ZrO₂ (rare earth stabilized CZ, Ce/Zr = 1/2, BET surface area: 45 m² g⁻¹) at a weight ratio of 1:1. The catalysts were aged at 1000 °C for 10 h under steady-state (rich, stoichi. and lean) and cyclic (rich/lean) conditions. The ageing gas contained a stoichiometric ratio of 1500 ppm of NO, 333 ppm of C₆H₆, 0.25 % of O₂, 0.35 % of CO, 10 % of H₂O, and balance of N₂. Rich conditions used reducing gas (+0.3 % CO) instead of stoichiometric gas. Lean conditions used oxidizing gas (+0.15 % O₂) instead of stoichiometric gas. Cycle ageing was carried out under rich (+0.3 % CO) and lean (+0.15 % O₂) conditions at a frequency of 0.5 Hz.

The catalytic activity test was carried out using a fixed-bed continuous-flow reactor. The 25 mg catalyst sample was mixed with 25 mg SiC powder, and then secured in a quartz tube (10 mm i.d.) by packing quartz wool at both ends of the catalyst bed. The reaction gas was a stoichiometric mixture of 1500 ppm of NO, 333 ppm of C₆H₆, 0.25 % of O₂, 0.35 % of CO, 10 % of H₂O, and balance of N₂. Cyclic conditions used oxidizing (+0.15 % or 0.3 % O₂) or reducing gases (+0.3 % or 0.6 % CO) alternately introduced to the steady-state reaction gas at a frequency of 0.5 Hz. The flow rate of the reaction gas was 500 cm³ min⁻¹. The catalytic activity was measured as the temperature was raised from 100 to 600 °C at 10 °C min⁻¹. The concentrations of NO, O₂, CO and CO₂ and the total hydrocarbons in the effluent gas were continuously monitored using on-line gas analyzers, HORIBA, Ltd., PG-240 and Shimadzu Corp., VMS-1000F, respectively. Rh dispersion was evaluated from the amount of CO chemisorption measured with a pulse method, assuming 1.0 CO/Rh stoichiometry. The sample was first reduced with H₂ at 400 °C for 1 h and then cooled to room temperature in flowing He. Several pulses of CO were introduced into the sample until no more adsorption was observed. H₂-TPR measurements were carried out to estimate the reducibility of the catalysts. All catalyst samples (50 mg) were measured without pretreatment. The temperature was raised to 700 °C at 10 °C min⁻¹ under 5 % H₂/Ar flow. H₂ consumption was monitored using a thermal conductivity detector (TCD). X-ray diffraction (XRD) patterns were observed using a X’Pert PRO (Pye) with Cu Kα radiation at 45 kV and 40 mA.

FT-IR spectra of adsorbed CO as a probe molecule were observed with a JASCO FT-IR-4200 at a resolution of 4 cm⁻¹. A self-supporting sample disk of about 25 mg cm⁻² was placed in an IR cell with CaF₂ windows and pretreated with 40 kPa of hydrogen at 400 °C for 1 h and then evacuated at the same temperature. The activated samples were contacted with 0.6 kPa of CO at room temperature and then the IR spectra were recorded.

3. Results and Discussion

3.1 Physico-chemical Properties of “Rh/Al + CZ”

Figure 1 shows the XRD patterns of “Rh/Al+ CZ” aged under different atmospheres. Distinct XRD peaks assigned to either cubic or metastable tetragonal (t”) phases of CeZrO₃ solid solution were observed for the fresh catalyst. Quite different XRD patterns were obtained for aged catalysts. All peaks became narrower and sharper after high-temperature ageing, indicating aggregation of CeZrO₃ solid solution. Two distinct peaks due to cubic and tetragonal CeZrO₃ were observed at lower and higher angles, respectively, compared with those of fresh catalyst. CeZrO₃ solid solution might be segregated into cubic CeO₂-rich and tetragonal ZrO₂-rich phases during high-temperature ageing. Phase segregation seems to be more prominent in rich and stoichiometric atmospheres. XRD patterns contained no peaks due to Rh species, suggesting Rh species were present in the amorphous and/or high dispersion states with sizes less than the XRD detection limit.

Rh dispersion was evaluated by CO chemisorption. Fresh catalyst has a big advantage of Rh dispersion...
The amount of CO adsorption expressed as CO/Rh exceeded unity, probably due to high dispersion of Rh species, resulting in the formation of dicarboxyl (Rh(CO)\textsubscript{2}) species with 2.0 CO/Rh stoichiometry\textsuperscript{28}. After high-temperature ageing as seen in Table 1, Rh dispersion in aged catalysts decreased in the order of stoichi. > rich > rich/lean > lean.

### 3.2. Light-off Performance of “Rh/Al+CZ”

The catalytic activity of “Rh/Al+CZ” aged under different atmospheres was evaluated in dynamic conditions (+0.3\% CO/0.15\% O\textsubscript{2}). The light-off curves are shown in Fig. 2. Deactivation of “Rh/Al+CZ” by high-temperature ageing was clearly observed. The light-off temperature at which 50\% conversion was achieved (T\textsubscript{50}) using “Rh/Al+CZ” was increased in the order of fresh < stoichi. ≈ rich < rich/lean < lean (Table 1), in accordance with the results of Rh dispersion. Therefore, “Rh/Al+CZ” with low Rh dispersion shows low light-off performance. Stoichi.-aged catalyst showed higher light-off performance than rich/lean-aged catalyst, although the mean gas composition was equivalent for both ageing treatments.

The TWC performance of Rh catalyst is known to strongly depend on the oxidation state. Catalysts with Rh species in the reduced state show high TWC performance\textsuperscript{29,30}. Therefore, the oxidation state of Rh species in “Rh/Al+CZ” was evaluated by in-situ FT-IR spectroscopy following CO adsorption. Figure 3 shows the FT-IR spectra of CO species adsorbed on Rh in “Rh/Al+CZ.” Peaks assigned to gem-dicarboxyl species on Rh\textsuperscript{+} (Rh\textsuperscript{+} (CO)\textsubscript{2})\textsuperscript{31,32} at 2024 cm\textsuperscript{-1} and 2099 cm\textsuperscript{-1} along with a shoulder peak due to linearly bonded CO on Rh\textsuperscript{2+} (Rh\textsuperscript{2+} (CO)\textsubscript{2})\textsuperscript{33,34} at 2075 cm\textsuperscript{-1} were observed for the fresh catalyst. Appearance of the bands due to gem-dicarboxyl and linearly bonded CO species depends on the Rh content in Rh/Al\textsubscript{2}O\textsubscript{3}\textsuperscript{35}. The IR band due to linearly bonded CO species is stronger in Rh/Al\textsubscript{2}O\textsubscript{3} with higher Rh content. Isolated Rh sites have IR spectra characteristic of Rh\textsuperscript{+} (CO)\textsubscript{2} species\textsuperscript{36}. In other words, highly dispersed Rh is favorable for the formation of Rh\textsuperscript{+} (CO)\textsubscript{2} species. Therefore, the appearance of Rh\textsuperscript{+} (CO)\textsubscript{2} species in fresh catalyst is due to the high dispersion of Rh (Table 1). Rich-, stoichi.-, and rich/lean-aged catalysts showed an IR band due to Rh\textsuperscript{2+}CO species at around 2075 cm\textsuperscript{-1}, suggesting similar surface oxidation state of Rh (Fig. 3). However, very weak shoulder peaks ascribed to Rh\textsuperscript{2+} (CO)\textsubscript{2} species were also observed for rich- and stoichi.-aged catalysts. The presence of isolated Rh sites despite the small amounts in rich- and stoichi.-aged catalysts would be related to the lower activation energy compared with “Rh/Al+CZ” might be promoted by contact with lean gas at 1000 °C even with a short contact time (10 s).

To investigate the difference in the catalytic activity of aged “Rh/Al+CZ,” the apparent activation energies for CO/C\textsubscript{3}H\textsubscript{6} oxidation and NO reduction were evaluated from the slope of Arrhenius plot in the temperature range of 230-270 °C, where reaction rate measured under nearly differential conditions achieved conversion efficiency below 30\%. Rich- and stoichi.-aged catalysts showed similar activation energy for all reactions, suggesting similar catalytically active sites and reaction mechanisms (Table 1). On the other hand, lean- and rich/lean-aged catalysts had higher activation energy than rich- and stoichi.-aged catalysts. As mentioned above, the status of Rh species in “Rh/Al+CZ” might be altered by treatment with lean gas at 1000 °C.

### Table 1 Light-off Activity (T\textsubscript{50}) and Apparent Activation Energy for TWC Reactions and Rh Dispersion in “Rh/Al+CZ” after High-temperature Ageing

| Ageing atmosphere | Light-off activity, T\textsubscript{50}, [°C] for | Apparent activation energy [kJ mol\textsuperscript{-1}] for | Rh dispersion [CO/Rh] |
|------------------|---------------------------------|---------------------------------|----------------------|
|                  | CO oxidation | C\textsubscript{3}H\textsubscript{6} oxidation | NO reduction | CO oxidation | C\textsubscript{3}H\textsubscript{6} oxidation | NO reduction |                  |
| fresh             | 208          | 264                                      | 238                | n.d.         | n.d.          | n.d.                | 1.23              |
| rich              | 250          | 293                                      | 256                | 61.5         | 204           | 81.2                | 0.07              |
| stoichi.          | 251          | 295                                      | 256                | 60.4         | 201           | 82.3                | 0.07              |
| lean              | 302          | 342                                      | 294                | 109          | 190           | 124                 | 0.01              |
| rich/lean         | 277          | 319                                      | 272                | 103          | 233           | 116                 | 0.03              |
Rh/lean-aged catalyst. On the other hand, unresolved and very weak IR bands were observed for lean-aged catalyst. The surface oxidation state of Rh would be difficult to correctly determine, but the morphology of Rh particles is suspected to be different from those in other aged catalysts. The surface oxidation state and the morphology of Rh particles probably to determine the light-off performance in TWC reactions.

3.3. NO Reduction Activity in High-temperature Region

NO conversion on aged “Rh/Al + CZ” did not reach 100% even at temperatures above 500°C, although CO and C₃H₆ conversions reached to 100% (Fig. 2). High NO conversion efficiency in high temperature regions under lean/rich perturbation conditions is related to the participation of OSC⁴,¹³). In other words, the PGM-CZ interaction is important in NO reduction under lean/rich perturbation conditions. To consider the possibility of the creation of Rh-CZ interactions by the ageing treatment, NO conversion efficiencies at 500 °C measured under steady-state and two different dynamic conditions, +0.3% CO/+0.15% O₂ and +0.6% CO/+0.3% O₂, were compared for rich-, stoichi.-, lean- and rich/lean-aged catalysts. All catalysts achieved 100% NO conversion efficiency under the steady-state condition (Fig. 4), which suggests that the effect of Rh dispersion on the NO conversion efficiency is not so prominent. Higher CO and O₂ concentrations under dynamic conditions resulted in large
deteriorations for stoichi., lean- and rich/lean-aged catalysts. However, relatively high NO conversion, which is comparable with that on rich-aged catalyst, was achieved on rich/lean-aged catalyst in a narrow rich/lean range (+0.3% CO+/0.15% O2). The frequency of IR bands due to CO species linearly bonded on Rh0 (ca. 2070 cm⁻¹) was slightly different depending on the ageing atmosphere (Fig. 3). The order of NO conversion at 500 °C seems to be consistent with the frequency of the IR band. Therefore, both the OSC properties, as discussed later, and the surface electric state of Rh are important factors affecting the NO reduction activity under the dynamic condition in a narrow rich/lean range. However, rich-aged catalyst still showed higher NO conversion even under dynamic conditions in a wide rich/lean range (+0.6% CO+/0.3% O2), suggesting the contribution of the OSC properties was more prominent. Rh-CZ interactions might also be newly created during ageing treatment under a rich atmosphere at 1000 °C.

The reducibility of Rh species is expected to be affected by the interactions with the support material. H2-TPR measurements were performed to investigate the reducibility of "Rh/Al + CZ" aged under different atmospheres. Fresh catalyst showed a distinct H2 consumption peak at 240 °C along with a shoulder peak at 130 °C and broad peak in the range of 300-650 °C (Fig. 5(a)). H2 consumption peaks below 300 °C were also observed for Rh/Al (Fig. 5(b)). These peaks are assigned to the consecutive reduction of Rh³⁺ to Rh⁰ [2,37,38]. The end of H2 consumption by fresh catalyst, around 650 °C, is similar to that of CZ. Therefore, the broad peak in the range of 300-650 °C may be due to the reduction of CZ. Appearance of a broad peak with a shift to lower temperature, compared with CZ, may indicate the creation of weak Rh-CZ interactions despite rough mixing of Rh/Al and CZ, because the reducibility of CZ is known to be promoted by contact with PGM [31,38].

Rich-, stoichi.- and rich/lean-aged catalysts showed a very weak reduction peak around 70 °C, which can be assigned to reduction of the RhOx surface (Fig. 5(a)). The weak intensity is probably because the Rh species are reduced during high-temperature ageing. This assumption might be supported by the fact that lean-aged catalyst showed an intense peak, which suggests the presence of Rh species in the oxidized state, at 110 °C. The H2 consumption peak at 240 °C for fresh catalyst was clearly shifted to higher temperature after high-temperature ageing, suggesting a change in the Rh-Al interaction. The peak observed for aged "Rh/Al + CZ" catalysts was located at higher temperature compared with that for Rh/CZ (Fig. 5(b)). The formation of strong Rh-CZ interactions by ageing seems not to have occurred.
The shape of the broad peak in the range of 300-650 °C was significantly changed depending on the ageing atmosphere. Rh species, which have little interaction with the support, are easily reduced at lower temperature, whereas Rh species with strong support interaction are reduced at higher temperature\(^{(29)}\). Therefore, a shift of the broad peak in the range of 300-650 °C, which may be due to the reduction of CZ, suggests the creation of weak Rh-CZ interactions with different strengths. Stoichi.- and rich/lean-aged catalysts had a very broad peak at the center of 450 °C (Fig. 5(a)). Rich- and lean-aged catalysts showed a shift of the broad peak to lower temperature, suggesting the creation of a slightly stronger Rh-CZ interaction compared with the stoichi.- and rich/lean-aged catalysts. Reduction of Rh-CZ in the rich-aged catalyst was completed at lower temperature compared with the lean-aged catalyst. The distribution of Rh-CZ interactions in the former catalyst seems to be relatively homogeneous. The \(\text{H}_2\text{-TPR}\) profile of Rh/Nd\(_{2}\)O\(_3\)-ZrO\(_2\) suggested the presence of three-dimensional, two-dimensional Rh\(_2\)O\(_3\) and Rh species interacting strongly with Nd\(_2\)O\(_3\), which were gradually reduced from low temperature\(^{(20,41)}\). Therefore, the morphology of Rh particles is suspected to depend on the ageing atmosphere. Two-dimensional Rh particles might be formed during rich ageing. Further experiments such as high-resolution TEM and element mapping are needed to reveal the morphology of the Rh particles.

The interface between PGM and support material may be important as catalytically active sites in TWC reactions\(^{(42)\text{-}44)}\). Differences in the Rh-CZ interactions may cause different contributions of OSC to NO reduction in high temperature regions. Therefore, the higher NO conversion on rich-aged catalyst observed under dynamic conditions with a wide rich/lean range (Fig. 4) can be explained by the formation of relatively strong Rh-CZ interactions during ageing.

### 4. Conclusions

The effect of the ageing atmosphere on the catalytic performance of “Rh/Al + CZ” for TWC reactions was investigated. Deactivation of “Rh/Al + CZ” was clearly observed irrespective of the ageing atmosphere. Lean-ageing caused significant deterioration of the light-off performance. Rh dispersion and light-off performance showed a good correlation. \(\text{In-situ} \ FT-\text{IR}\) spectroscopy following CO adsorption revealed the presence of isolated Rh sites in rich- and stoichi.-aged catalysts, which showed better light-off performance among the aged catalysts. The surface oxidation state and the morphology of the Rh particles were responsible for the light-off performance in TWC reactions. NO conversion on aged “Rh/Al + CZ” did not reach 100 % even above 500 °C under lean/rich perturbation conditions. Higher CO and O\(_2\) concentrations under dynamic conditions resulted in large deteriorations for lean- and rich/lean-aged catalysts, but rich-aged catalyst showed higher NO conversion. H\(_2\)-TPR measurements showed the formation of relatively strong Rh-CZ interactions in rich-aged catalyst, which was responsible for the higher NO conversion under dynamic conditions with a wide rich/lean range.

### References

1) Rood, S., Eslava, S., Manigrasso, A., Bannister, C., \(\text{Proc. IMechE Part D: J Auto. Eng.}, 234\), 936 (2020).
2) Zheng, Q., Farraruto, R., Deeba, M., Valsamakis, I., \(\text{Catalysts, 5}\), 1770 (2015).
3) Whittington, B. I., Jiang, C. J., Trimm, D. L., \(\text{Catal. Today}, 26\), 41 (1995).
4) Barbier Jr., J., Duprez, D., \(\text{Appl. Catal. B: Environ.}, 4\), 105 (1994).
5) Weibel, M., Garin, F., Bernhardt, P., Maires, P., Prignet, M., \(\text{Stud. Surf. Sci. Catal.}, 71\), 195 (1991).
6) Engler, B., Koberstein, E., Lindner, D., Lux, E., \(\text{Stud. Surf. Sci. Catal.}, 71\), 641 (1991).
7) Tanabe, T., Morikawa, A., Hatanaka, M., Takahashi, N., Nagai, Y., Sato, A., Kuno, O., Suzuki, H., Shinjoh, H., \(\text{Catal. Todday}, 184\), 219 (2012).
8) Wang, Q., Zhao, B., Li, G., Zhou, R., \(\text{Environ. Sci. Technol.}, 44\), 3870 (2010).
9) Shen, M., Yang, M., Wang, J., Wen, J., Zhao, M., Wang, W., \(\text{J. Phys. Chem. C}, 113\), 3213 (2009).
10) Haneda, M., Tomida, Y., Sawada, H., Hattori, M., \(\text{Top Catal.}, 59\), 1059 (2016).
11) Goula, G., Botzolakis, G., Osatashitani, A., Parlett, C. M. A., Kyriakou, G., Lambert, R. M., Yentekakis, I. V., \(\text{Catalysts, 9}\), 541 (2019).
12) Shelef, M., Graham, G. W., \(\text{Catal. Rev. Sci. Eng.}, 36\), 433 (1994).
13) Trovarelli, A., \(\text{Catal. Rev. Sci. Eng.}, 38\), 439 (1996).
14) Burch, R., \(\text{Catal. Rev.}, 46\), 271 (2004).
15) Tomida, Y., Haneda, M., \(\text{Catal. Today}, 59\), in press.
16) Kašpar, J., Fornasiero, P., Graziani, M., \(\text{Catal. Today}, 50\), 285 (1999).
17) Haneda, M., Shinoda, K., Nagane, A., Houshito, O., Takagi, H., Nakahara, Y., Hiroe, K., Fujitani, T., Hamada, H., \(\text{J. Catal.}, 259\), 223 (2008).
18) Kihis, L. S., Stadnichenko, A. I., Kocshev, S. V., ZaiKovskii, V. L. Boronin, A. L., \(\text{J. Phys. Chem. C}, 120\), 19142 (2016).
19) Machida, M., Eidone, T., Minami, S., Buwono, H. P., Hinokuma, S., Nagao, Y., Nakahara, Y., \(\text{J. Phys. Chem. C}, 119\), 11653 (2015).
20) Kawabata, H., Koda, Y., Sumida, H., Shigetsu, M., Takami, A., Inumaru, K., \(\text{Catal. Sci. Technol.}, 4\), 697 (2014).
21) Haneda, M., Tomida, Y., Takahashi, T., Azuma, Y., Fujimoto, T., \(\text{Catal. Commun.}, 90\), 1 (2017).
22) Nagao, Y., Nakahara, Y., Sato, T., Iwakura, T., Takeshita, S., Minami, S., Yoshida, H., Machida, M., \(\text{ACS Catal.}, 5\), 1986 (2015).
23) Kawabata, H., Koda, Y., Sumida, H., Shigetsu, M., Takami, A., Inumaru, K., \(\text{Catal. Sci. Technol.}, 5\), 584 (2015).
24) Suhonen, S., Valden, M., Hiitikko, M., Laitinen, R., Savimaki, A., Härkönen, M., \(\text{Appl. Catal. A: General}, 218\), 151 (2001).
25) Monte, R. D., Kašpar, J., \(\text{J. Mater. Chem.}, 15\), 633 (2005).
26) Li, J., Liu, X., Zhan, W., Guo, Y., Guo, Y., Lu, G., \(\text{Catal. Sci. Technol.}, 6\), 897 (2016).
27) Zhou, C., Zhang, H., Zhang, Z., Li, L., \(\text{Appl. Surf. Sci.}, 539\).
要 旨

担持ロジウム触媒の三元触媒活性に及ぼす熱処理ガス条件の影響

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実触媒を想定した Rh/Al2O3 と CeO2−ZrO2 (CZ) を複合化した触媒の三元触媒活性に及ぼす熱処理ガス条件の影響を検討した。 Ritch, ストイキ、リーンおよびRitch/リーン変動条件での熱処理によりライトオフ活性は低下したが、その活性順列は Fresh > Ritch > Ritch/リーン変動 > リーンとなった。活性の序列は Rh 分散度と一致したが、定量的な一致は見られなかった。吸着 CO 種の IR 測定より、dicarbonyl 種が生成する孤立した Rh サイトの存在が高儀ライトオフ活性の発現に寄与することが明らかとなった。また、Ritch/リーン変動条件における高温域での NO 転化率は熱処理ガス条件の影響を強く受けることが分かった。H2-TPR の結果、熱処理によ り Rh-CZ 相互作用が成熱されること、相互作用の強さは熱処理ガス条件により異なること、相互作用が強くほど高温域での NO 転化率が高く維持されることが明らかとなった。