Broadening of the effective temperature range for NO removal on Co·Pd-modified H-ZSM-5 catalyst by suppression of CH_4 combustion

Koji Kagawa, Yoko Ichikawa, Shinji Iwamoto and Tomoyuki Inui *

Department of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-8501, Japan
E-mail: inui@scl.kyoto-u.ac.jp

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Broadening the effective temperature range (window) of NO removal on Co·Pd-modified H-ZSM-5 (Co/Pd/H-ZSM-5) in the presence of methane under an excess-oxygen condition was tried under the concept that the lack of the amount of methane occurred by CH_4 combustion at high temperature reduced NO conversion to N_2. The activity for NO removal of the catalyst at high temperature was improved due to suppression of methane combustion by the thermal treatment of Pd in a H_2-containing flow. Co/Pd/H-ZSM-5s with and without the thermal treatment of Pd showed different temperature windows for NO elimination. These different windows were then combined by a two-stage catalyst packing, in which Co/(Pd/H-ZSM-5)$_{red.}$ and Co/Pd/H-ZSM-5 were placed in series, resulting in the broadening of the window.

Keywords: Co·Pd-modified H-ZSM-5, two-stage catalyst packing, thermal treatment, CH_4 combustion, NO elimination

1. Introduction

Nitric oxide is one of the major components of air pollution, which become the source of photochemical smog and acid rain. The removal of NO in exhaust gases from motor vehicles equipped with gasoline engines has been successfully performed by ‘three-way catalysts’, which consist of Rh, Pt and Pd, supported on a ceramic monolith [1]. However, these kinds of catalysts can only exhibit their best performances under very limited conditions, i.e., so-called ‘window’, however, under an excess-oxygen condition, they do not work well for removal of NO. As for the countermeasure against the emission of nitric oxides (NOx) from stationary facilities, a process of ‘selective catalytic reduction’ (SCR) is adopted commercially [2], using mixed oxide catalysts such as vanadia-tungstine on titania support, and NH_3 is used as the reductant. Although removal of NO can be achieved even under the presence of oxygen by this process, it has still many problems to be overcome such as disadvantages in the transportation and storage of NH_3, the emissions of unreacted NH_3, the corrosion of equipment by the contact of NH_3, the blockage of the pipes in facilities by ammonia sulfates, and the high equipment cost. Therefore, a process for the removal of NO using more convenient and safe reductants other than NH_3 is strongly demanded.

Several years ago, significant studies on the removal of NO under an excess-oxygen condition in the presence of hydrocarbons were reported using zeolitic catalysts [3–6]. If methane can be used as the reductant instead of NH_3, it will offer a better system, because natural gas, in which methane is the main component, is readily available and widely used as a fuel for the boiler and gas turbine in the generation and cogeneration system for electricity, and more convenient and economical than NH_3. A copper-ion-exchanged H-ZSM-5 (Cu/H-ZSM-5), which showed a high activity for the removal of NO in the presence of oxygen and propane or propene, has been studied extensively from the aspect of reaction mechanism [7,8], zeolite structure [8,9], and deactivation [10,11]. However, Cu/H-ZSM-5 was inactive when methane was adopted as the hydrocarbon to be added [12]. Armor and co-workers [13,14] reported that cobalt-ion-exchanged H-ZSM-5 (Co/H-ZSM-5) was a very active catalyst for the removal of NO in the presence of methane and had high thermal stability. Palladium-ion-exchanged H-ZSM-5 (Pd/H-ZSM-5) was also reported as the effective catalyst for this reaction by Nishizaka and Misono [15]. In other previous studies, H-ZSM-5 ion-exchanged with both Pd and Co showed a high catalytic performance for conversion of a low concentration NOx, even when the reaction gas contains steam [16]. Furthermore, conversion of NO on this catalyst was higher than on Ir/In/H-ZSM-5 [17], which was reported as an effective catalyst by Kikuchi and Yogo [18]. In the case of [17], conversion of NO decreased above 450 °C with elevating temperature. In general, the reaction factors, such as temperature, pressure, and the kind and concentration of reactants, were established to obtain the maximum yield of the intended products in the case of catalytic processes. On the other hand, for the purpose of environmental protection, especially for cleaning up the flue-gas, there is no choice to pre-arrange the reaction conditions. From this view-point, it is important to expand the effective temperature range for the removal of NO.

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* To whom correspondence should be addressed.

In this study, the expansion of the effective temperature range for removal of NO in the presence of methane was tried using H-ZSM-5 loaded with both Co and Pd by the ion-exchange method (Co/Pd/H-ZSM-5). The lack of available methane in the reactants by the predominate combustion at high temperatures reduces conversion of NO. Therefore, the activity for the removal of NO at high temperature was improved by suppressing the combustion of CH_4 by the appropriate sintering of Pd by a high-temperature treatment in H_2-containing gas. Since it was reported [19] that the effective temperature range for the removal of NO could be expanded by the proper combination of catalysts having a different temperature window, combination of Co/Pd/H-ZSM-5s with and without the thermal treatment of Pd/H-ZSM-5 was also investigated.

2. Experimental

2.1. Catalyst preparation

Protonated ZSM-5 was prepared by the rapid crystallization method [20]. Its Si/Al atomic ratio was 22. Loading of Pd on H-ZSM-5 was carried out by ion-exchange method as follows: a 3 g portion of H-ZSM-5 was put into 100 ml of 4.3×10^{-4} M $Pd(NH_3)_4(NO_3)_2$ aqueous solution and was heated at 80 °C for 24 h while stirring with a magnetic stirrer. It was washed, dried, followed by calcination at 540 °C for 3.5 h in air. Various degrees of cobalt-ion exchange for this catalyst were made by the same way using 0.26, 0.52, or 1.04 mM $(CH_3COO)_2Co$ aqueous solutions at 80 °C. In the case of Co/Pd/H-ZSM-5, the ion exchanges were done in the order of Pd then Co.

The thermal treatment of Pd/H-ZSM-5 was carried out as follows: it was heated in N_2 flow from room temperature to 500 °C within 1 h with a constant heating rate, and then the N_2 flow was replaced by a 10% H_2-containing N_2 flow, and was kept for 30 min at that temperature. It had been confirmed that the structure of H-ZSM-5 was not affected at that temperature [21]. The catalyst treated at 500 °C in H_2 was designed as $(Pd/H/ZSM\text{-}5)_{red.}$.

The catalyst in powder form was tabletted by a tablet machine. It was crushed and sieved by 12–22 mesh to provide the reaction.

The chemical compositions of the catalysts were analyzed by inductively coupled plasma (ICP; Shimadzu ICPS-1000 III), as shown in table 1.

Table 1
Chemical composition of the catalysts measured by ICP.

	Catalyst	Co		Pd	
		wt%	Co/Al	wt%	Pd/Al
Cat. 1	Co/H-ZSM-5	0.34	0.10	–	–
Cat. 2	Co/H-ZSM-5	0.80	0.20	–	–
Cat. 3	Co/H-ZSM-5	1.78	0.49	–	–
Cat. 4	Pd/H-ZSM-5	–	–	0.09	0.01
Cat. 5	Co/Pd/H-ZSM-5	0.69	0.21	0.06	0.01
Cat. 6	$Co/(Pd/H\text{-}ZSM\text{-}5)_{red.}$	0.72	0.18	0.08	0.01

2.2. Reaction

Performance of the catalysts for NO removal was examined using an ordinary flow reactor under atmospheric pressure. A 0.7 g (ca. 1.2 ml) portion of the catalyst was packed in a quartz tubular reactor of 9 mm inner diameter. After preheating in He flow at 600 °C for 30 min, the catalytic performance was measured at every 50 °C from 600 to 200 °C. The reaction gas containing 1,000 ppm NO, 3,000 ppm CH_4, and 2.0% O_2, diluted with He, was allowed to flow through the catalyst bed with decreasing the temperature. At each temperature, the outlet gas of 10 min on stream was analyzed by gas chromatographs (Chrompack, Micro GC CP 2002 with MS-5A and Porapack Q columns) equipped with integrators. Catalytic activities for CH_4 combustion and NO removal were evaluated by conversion of CH_4 to $CO + CO_2$ (COx) and conversion of NO to N_2, respectively. Although N_2O in products was analyzed, the conversion of NO to N_2O was less than 2.8%.

3. Results and discussion

The effect of the amount of Co loading on the catalytic activity for NO-elimination reaction is shown in figure 1. Conversion of CH_4 to COx and the maximum NO conversion to N_2 increased with an increase in the Co content. In cases of cats. 2 and 3, conversion of NO to N_2 increased with elevating reaction temperature from 200 to 500 °C,

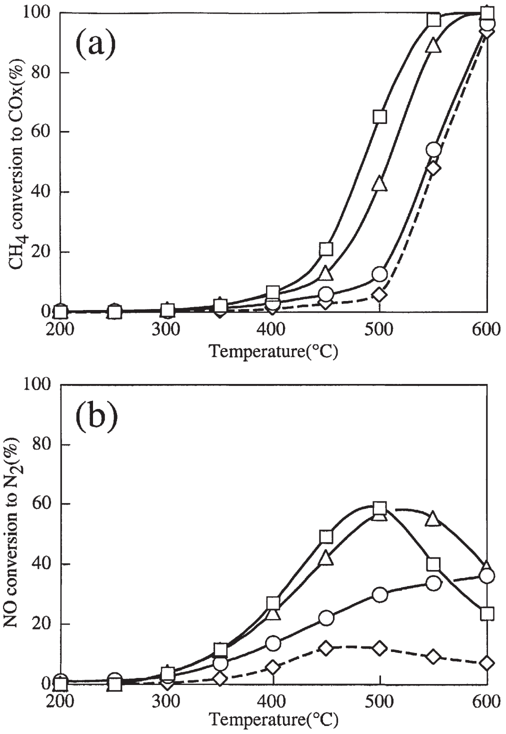


Figure 1. Effect of the amount of Co loading on catalytic activity for NO-elimination reaction. (a) CH_4 conversion to COx, (b) NO conversion to N_2. (○) Cat. 1 (Co 0.34 wt%), (△) cat. 2 (Co 0.80 wt%), (□) cat. 3 (Co 1.78 wt%), (◇) H-ZSM-5. Feed gas: NO 1,000 ppm, CH_4 3,000 ppm, O_2 2.0%, He balance, SV 10,000 h^{-1}.

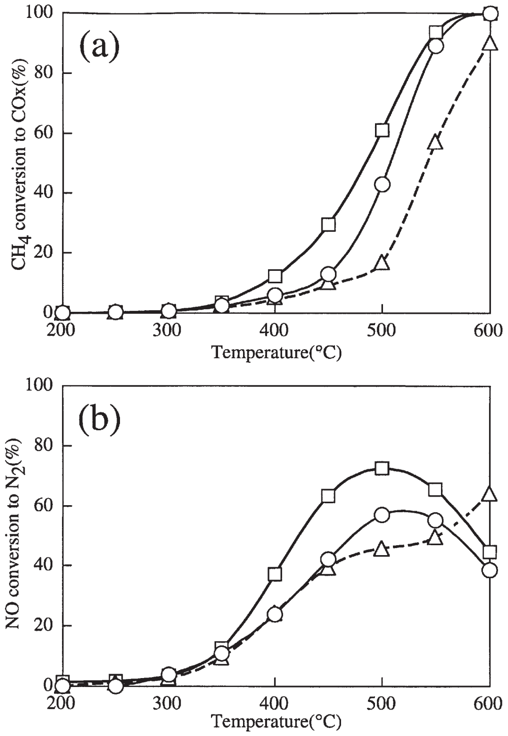


Figure 2. Catalytic activities of Co/H-ZSM-5 (cat. 2), Pd/H-ZSM-5 (cat. 4), and Co/Pd/H-ZSM-5 (cat. 5) for NO-elimination reaction. (a) CH_4 conversion to COx, (b) NO conversion to N_2. (○) Cat. 2, (△) cat. 4, (□) cat. 5. Feed gas: NO 1,000 ppm, CH_4 3,000 ppm, O_2 2.0%, He balance, SV 10,000 h^{-1}.

and decreased above 500 °C. This decrease above 500 °C can be explained by the lack of CH_4 in the reactant caused by CH_4 combustion.

Figure 2 shows catalytic activities on Co/H-ZSM-5 (cat. 2), Pd/H-ZSM-5 (cat. 4), and Co/Pd/H-ZSM-5 (cat. 5). Conversion of CH_4 and NO on Co/Pd/H-ZSM-5 were enhanced in a wide temperature range from 350 to 550 °C by a synergistic effect due to co-existence of Pd and Co on H-ZSM-5. However, NO conversion decreased at the temperature above 500 °C due to the lack of CH_4 in the reactants. Ogura et al. [17] reported a similar synergistic effect caused by Pd and Co on H-ZSM-5 for the NO elimination reaction under a low NO concentration (100 ppm), and observed the decrease of NO conversion above 400 °C, but the reason of this decrease was not described.

Since the decrease of NO conversion at high temperature range might be moderated by the suppression of the activity of Pd for CH_4 combustion, thermal treatment of the catalyst was carried out to reduce the activity by sintering of Pd. Cobalt was ion-exchanged after the thermal treatment of Pd/H-ZSM-5 to avoid the influence of this treatment to Co. The effect of the thermal treatment on the catalytic activity of Pd/H-ZSM-5 is shown in figure 3. Both conversions of CH_4 and NO at above 450 °C decreased by the thermal treatment. Below 450 °C, the activities of both catalysts coincided each other. Consequently, it was expected that CH_4 combustion for Co/(Pd/H-ZSM-5)$_{red.}$ was suppressed

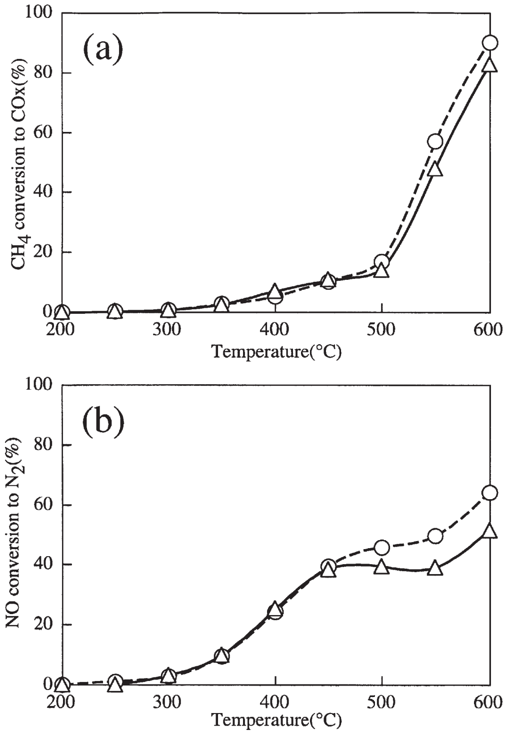


Figure 3. Effect of the thermal treatment on the catalytic activity of Pd/H-ZSM-5 (cat. 4) for NO-elimination reaction. (a) CH_4 conversion to COx, (b) NO conversion to N_2. (○) Pd/H-ZSM-5 (cat. 4), (△) (Pd/H-ZSM-5)$_{red.}$. Feed gas: NO 1,000 ppm, CH_4 3,000 ppm, O_2 2.0%, He balance, SV 10,000 h^{-1}.

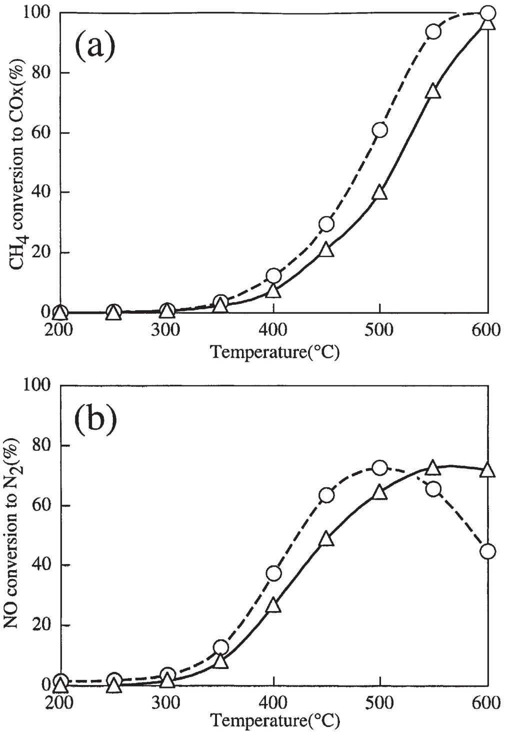
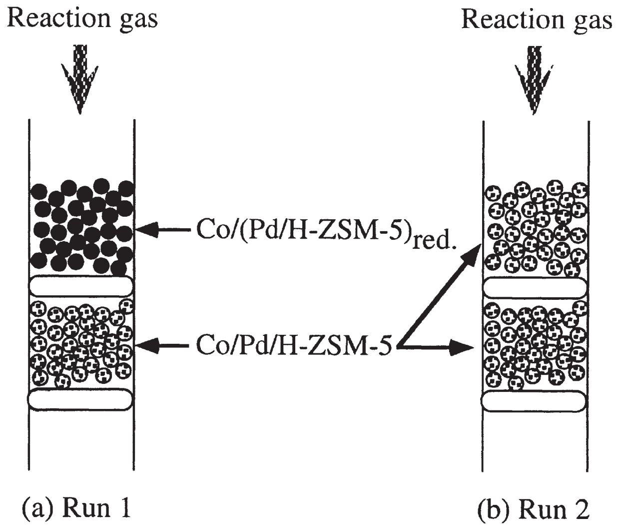


Figure 4. Effect of the thermal treatment of Pd/H-ZSM-5 on the catalytic activity of Co/Pd/H-ZSM-5 for NO-elimination reaction. (a) CH_4 conversion to COx, (b) NO conversion to N_2. (○) Co/Pd/H-ZSM-5 (cat. 5), (△) Co/(Pd/H-ZSM-5)$_{red.}$ (cat. 6). Feed gas: NO 1,000 ppm, CH_4 3,000 ppm, O_2 2.0%, He balance, SV 10,000 h^{-1}.

only above 450 °C, and NO conversion would increase and be maintained above and below 450 °C, respectively.

The catalytic activity of Co/(Pd/H-ZSM-5)$_{red.}$ is shown in figure 4, in comparison with Co/Pd/H-ZSM-5. Conversion of CH_4 decreased at the whole temperature range, and NO conversion above 550 °C increased by the suppression of CH_4 combustion, although NO conversion decreased below 450 °C, contrary to the expectation mentioned above. In order to combine high catalytic activities of Co/Pd/H-ZSM-5 below 500 °C and Co/(Pd/H-ZSM-5)$_{red.}$ above 550 °C, a two-stage catalyst packing as illustrated in figure 5(a) was applied. When Co/(Pd/H-ZSM-5)$_{red.}$ is placed before Co/Pd/H-ZSM-5, the catalytic activity for NO removal is expected to take place over a wider temperature range, which would be approximately the sum of the temperature windows of both catalysts. When these two kinds of catalysts are placed in reverse order, only the activity of Co/Pd/H-ZSM-5 is anticipated, because insufficient amount of CH_4 remains at the inlet of Co/(Pd/H-ZSM-5)$_{red.}$ layer at the temperature suitable for this catalyst. The effective temperature range for NO removal will be enlarged because CH_4 and NO unreacted in the first stage are supplied into the second stage. Figure 6 shows the effect of a two-stage catalyst packing of Co/(Pd/H-ZSM-5)$_{red.}$ and Co/Pd/H-ZSM-5. The profile of CH_4 conversion dose not show typical sigmoid curve. Above 450 °C, the suppression of CH_4 combustion was observed, and NO conversion attained to as high as 80%. Although NO conversion decreased at the temperature range above 550 °C, it was close to that of Co/(Pd/H-ZSM-5)$_{red.}$.



(a) Run 1
(b) Run 2

Figure 5. Illustration of a two-stage catalyst packing. (a) Run 1: Co/(Pd/H-ZSM-5)$_{red.}$ and Co/Pd/H-ZSM-5 were placed in the first and second stages, respectively. (b) Run 2: Co/Pd/H-ZSM-5 was placed in both stages.

The effect of space velocity (SV) on the catalytic activity of Co/Pd/H-ZSM-5 and the comparison between runs 1 and 2 are shown in figure 7. By increasing the packing amount of Co/Pd/H-ZSM-5, NO conversion increased at

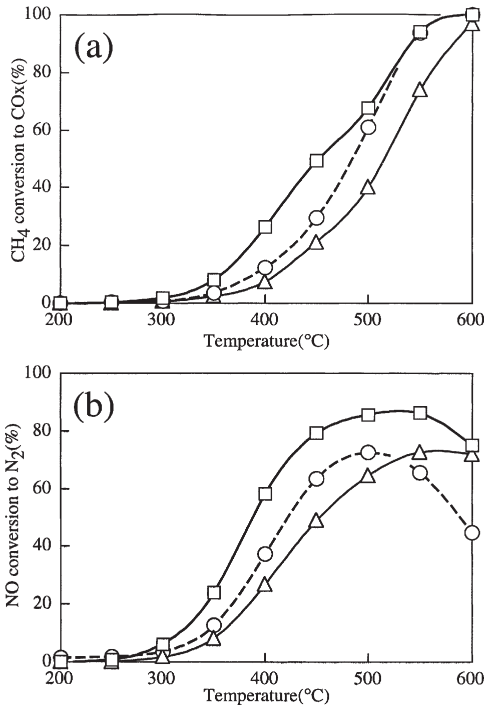


Figure 6. Effect of the combination of Co/Pd/H-ZSM-5 and Co/(Pd/H-ZSM-5)$_{red.}$. (a) CH_4 conversion to COx, (b) NO conversion to N_2. (○) Co/Pd/H-ZSM-5 (SV 10,000 h^{-1}), (△) Co/(Pd/H-ZSM-5)$_{red.}$ (SV 10,000 h^{-1}), (□) first-stage Co/(Pd/H-ZSM-5)$_{red.}$ + second-stage Co/Pd/H-ZSM-5 (SV 5,000 h^{-1}). Feed gas: NO 1,000 ppm, CH_4 3,000 ppm, O_2 2.0%, He balance.

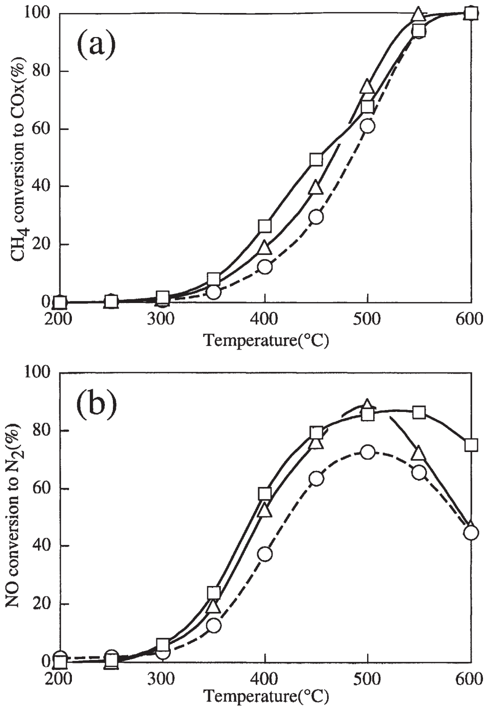


Figure 7. The effect of SV on the catalytic activity of Co/Pd/H-ZSM-5 and the comparison between run 1 and run 2. (a) CH_4 conversion to COx, (b) NO conversion to N_2. (○) Co/Pd/H-ZSM-5 (SV 10,000 h^{-1}), (△) Co/Pd/H-ZSM-5 (SV 5,000 h^{-1}), (□) first-stage Co/(Pd/H-ZSM-5)$_{red.}$ + second-stage Co/Pd/H-ZSM-5 (SV 5,000 h^{-1}). Feed gas: NO 1,000 ppm, CH_4 3,000 ppm, O_2 2.0%, He balance.

the whole temperature range and decreased above 500 °C. Although it was expected that CH_4 conversion of the two-stage catalyst packing at the whole temperature range and NO conversion below 500 °C would be less than those of run 2, conversions of CH_4 and NO of run 1 exceeded those of Co/Pd/H-ZSM-5 below 450 °C. Partial pressure dependencies for NO, CH_4, and O_2 at 400 °C on Pd/Co/H-ZSM-5 were reported as the orders of 0.1, 1.2, and 0.0, respectively [17]. The composition of outlet gases from Co/Pd/H-ZSM-5 or $\text{Co/(Pd/H-ZSM-5)}_{\text{red.}}$ in the first stage can be calculated from the results of these catalysts under the condition of $SV = 10{,}000\ h^{-1}$ shown in figure 4. The ratio of reaction rates in the second stage at 400 °C in cases of runs 1 and 2 was calculated from these reaction orders and the gas compositions. The reaction rate in the second stage of run 1 is 1.1 times as large as that of run 2. These results demonstrate that the combination of Co/Pd/H-ZSM-5 and $\text{Co/(Pd/H-ZSM-5)}_{\text{red.}}$ successfully improves the performance for NO-elimination reaction by expanding the effective temperature range.

4. Conclusions

Combustion of CH_4 on Co/Pd/H-ZSM-5 was suppressed by the thermal treatment under the gas flow containing H_2 for Pd/H-ZSM-5. The decrease of NO conversion on Co/Pd/H-ZSM-5 above 500 °C was improved by the thermal treatment for Pd. However, NO conversion on this catalyst below 500 °C decreased. The different effective temperature windows for NO elimination of Co/Pd/H-ZSM-5 and $\text{Co/(Pd/H-ZSM-5)}_{\text{red.}}$ were combined by a two-stage catalyst packing in series way. The multi-stage reaction system, in which two or more catalyst components with different temperature windows are placed in a sequential form, would provide a more beneficial deNOx system in the presence of natural gas to the commercial application.

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