

Simultaneous Removal of NO and N_2O over Pd-ZSM-5 Catalysts and FT-IR Observations of their Decomposition Routes to N_2

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Simultaneous removal of nitrogen monoxide and dinitrogen oxide with propene was investigated over Pd-H-ZSM-5 catalysts. Results were compared with reports of simultaneous removal of NO and N_2O in the presence of O_2 over Co-ZSM-5 and Fe-MFI. The N_2O conversion was suppressed in the presence of NO, and the simultaneous removal rates were essentially the same as the NO conversion rates over Co-ZSM-5 and Fe-MFI. In contrast, the simultaneous removal in the presence of O_2 was found to be accelerated over Pd-H-ZSM-5 and conventional Pd/SiO_2 compared to the sum of the corresponding individual removal rates of NO and N_2O. An intense FT-IR peak of $NO^{\pm 0}$ ligated to the Pd cation inside the ZSM-5 cage was observed at 1868 cm^{-1} in the promoted simultaneous removal reactions. Under the conditions for the individual removal of NO or N_2O and the unpromoted simultaneous removal of NO + N_2O, only a weak peak at 1842 cm^{-1} was observed. The oxygen atom that dissociates from N_2O should be the key to promoted catalysis in the coexistence of NO and N_2O in order to maintain the Pd cation site clear. The oxygen controls the concentration of surface carbonaceous species to effectively decompose NO, and so as not to inhibit the NO activation.

The catalytic removal of nitrogen oxides has been intensively investigated in relation to environmental problems.[1] Eliminating nitrogen monoxide usually entails the formation of dinitrogen oxide as a by-product, which also affects the environment. In this context, simultaneous catalytic removal of NO and N_2O is a simplified and improved process for environmental catalysis. Simultaneous removal of NO and N_2O was reported on Co-ZSM-5[2] and on Fe-MFI catalysts.[3] Atmospheric oxygen and/or water often affects the rates of NO and/or N_2O catalytic removal.[2,3] It is important to investigate catalysts active in the presence of oxygen and/or water vapor. They are present in industrial situations where there is a need for NO and/or N_2O removal.

From a scientific point of view, the reaction mechanism of NO catalytic removal with reductants (e.g., hydrocarbons or ammonia) is rather complicated. This is because the process has the potential to form various intermediates and products; N_2, N_2O, NO_2, CO and CO_2 are all possible products when a hydrocarbon is utilized as a reductant. In contrast, if the simultaneous removal process allows us to selectively form N_2, the reaction mechanism should be relatively simple.

The Co-ZSM-5 catalyst is effective for both NO and N_2O removal. Simultaneous removal was tested on Co-ZSM-5 with methane in the presence of O_2 at 673–773 K, and the rates were essentially the same as those for the removal of NO alone.[2] In the simultaneous removal on Fe-MFI with propane in the presence of O_2 at 523 − 773 K, the NO conversion rates were similar to those for the individual conversion of NO, whereas the N_2O conversion rates were significantly suppressed when compared to the individual conversion of N_2O.[3] A common feature of these two metal-exchanged zeolites is that the NO conversions were not affected by the presence of N_2O, whereas the N_2O conversions were inhibited with the presence of NO.

In this paper, the simultaneous removal of NO and N_2O over Pd-H-ZSM-5 catalysts is reported and compared with results for Pd-Na-ZSM-5 and conventional Pd/SiO_2 catalysts. Palladium is one of the components of the three-way catalyst (Rh, Pt, Pd) for automobile exhaust gas. Because palladium generally activates hydrocarbons,[4–7] propene was chosen as the reductant for N_xO (x = 1, 2) rather than ammonia.[8] ZSM-5 has been widely investigated as an NO reduction catalyst by using hydrocarbons, especially as the metal-exchanged form.[2,4,7,9–11] The promoted simultaneous reactions rather than the sum of the individual removal rates of NO or N_2O are reported for Pd-H-ZSM-5 and Pd/SiO_2. The simplified reaction mechanisms (the routes from NO and N_2O to N_2) were monitored by in situ FT-IR (Fourier-transformed infrared) spectroscopy. The key features that affect the promotion of NO removal in the presence of N_2O are proposed.

Experimental

Catalyst Preparation. The Pd-H-ZSM-5 catalyst was prepared by continuously mixing 3.0 g of H-ZSM-5 and 0.10 g of palladium(II) nitrate in distilled water for 24 h. The mixture was filtrated and washed seven times with distilled water. The powder that was obtained was dried at 393 K for 12 h and heated in air at 673 K for 4 h. ICP (inductively coupled plasma) results demonstrated that all the Pd ions were incorporated in/on the zeolite (Pd 1.5 wt%). H-ZSM-5 was prepared by the ion exchange of Na-ZSM-5 (SiO_2/Al_2O_3 = 23.3, primary crystalline size 0.1–0.5 μm, Tosoh) with aqueous ammonium nitrate at 290 K for 24 h. ICP measurements revealed that 98% of the sodium sites were substituted with protons. The pore area of ZSM-5 is 5.3 by 5.6 Å or 5.1

by 5.5 Å, and the pore volume is 0.29 $cm^3\ g^{-1}$ based on the cyclohexane adsorption measurements. A Pd-Na-ZSM-5 catalyst was prepared from Na-ZSM-5 (Pd 1.6 wt% in dry sample) using a similar procedure. The atomic ratio of incorporated palladium atoms to Na^+ ions in Na-ZSM-5 before mixing with Pd^{2+} was 11%.

A conventional Pd/SiO_2 catalyst was prepared by the incipient impregnation method[12,13] by using silica (Davisson No. 952) and palladium(II) nitrate with distilled water. The powder that was obtained was dried at 393 K for 12 h and subsequently heated in air at 673 K for 4 h. The Pd loading was 0.5 wt%.

Kinetic Measurements. The catalytic removals of NO and/or N_2O were performed in a closed circulating system (117 cm^3) over either 0.12–0.16 g of Pd-H-ZSM-5 and Pd-Na-ZSM-5 or conventional Pd/SiO_2 catalysts. The flow rate of gas was 10–30 $cm^3\ min^{-1}$. A closed circulating system connected to a vacuum system was chosen rather than a conventional flow system in order to correlate the reactivity to infrared spectroscopic data obtained on a basis of vacuum cell + catalyst disk + reaction gas. Before catalysis, the catalysts were treated in oxygen (27 kPa) for 1h, in hydrogen (27 kPa) for 1 h, and finally under vacuum for 0.5 h at 653 K. The reaction gas pressures were 0.56, 0.56, 8.1, and 0.56 kPa for NO, N_2O, O_2, and propene, respectively. The remainder of the gas necessary to obtain a pressure of 101.3 kPa was made up with helium (balance). The combinations of reaction gases used were as follows: NO; NO + O_2; NO + C_3H_6; NO + O_2 + C_3H_6 (*individual* removal of NO); N_2O; N_2O + O_2; N_2O + C_3H_6; N_2O + O_2 + C_3H_6 (*individual* removal of N_2O); NO + N_2O; NO + N_2O + O_2; NO + N_2O + C_3H_6; and NO + N_2O + O_2 + C_3H_6 (*simultaneous* removal). Most of the kinetic measurements were performed with impurity moisture levels less than 0.01 kPa. A control experiment was done in the presence of 0.56 kPa water gas for Pd-H-ZSM-5 and Pd/SiO_2.

Molecular Sieve 5A (N_2, O_2, and CO) and Unibeads C (NO, N_2O, and CO_2) columns were utilized for GC analysis with a detector system of TCD (Shimadzu GC-8A). The reaction rates became constant within 1 h for all the reactions at 548 K. The reaction temperature was fixed, based on preliminary reactions: the formation rates of N_2 and O_2 reached the steady state and were maintained for more than 24 h at 548 K. The relatively low temperature was the compromise between high enough conversion and better quality of FT-IR data. Increasing temperature caused an increase in the conversion, but did decrease the *S*/*N* ratio and peak intensity of FT-IR spectra due to the larger background and desorption of surface species at > 600 K. Although a steady state can be realized only for zero-order reactions in a closed circulating system, the observed constant rates are nearly steady-state rates because catalysis occurred on Pd-H-ZSM-5 at relatively low temperature (548 K) and relatively low conversion. The (pseudo) steady-state rates were used in this work. The gas decrease induced by sampling was taken into account in estimating the reaction rate.

FT-IR Measurements. The FT-IR spectra were measured by a Jasco, Valor III (single beam configuration, energy resolution 1 cm^{-1}, MCD detector), in transmission mode with an in situ quartz glass cell (Fig. 1). The in situ cell, capped by sodium chloride windows,[14–19] was combined with a closed circulating system. Eighty milligrams of catalysts were pressed into a disk (ϕ = 20 mm). The temperature and ambient gas pressure for the sample disk can be controlled in the in situ cell within the limits of 173–823 K and 0–101.3 kPa, respectively. Gas phase spectra were measured using the in situ cell without a catalyst sample.

The sample disk was treated in the same procedure as for kinetic measurements. The sample was cooled down from 653 K (pretreatment) to 548 K (reaction temperature), and the reaction gas was introduced to the sample. The in situ spectra were measured at 548 K. After the introduction of reaction gas, the infrared peak intensity first increased and then saturated within 1–3 h. The spectra for the catalyst sample before the introduction of reaction gas were subtracted from the in situ spectra. Equivalent N_2 formation rates were obtained for NO/N_2O reactions with powder in a *U*-shaped tube in the closed circulating system as compared to pressed disk catalysts in an infrared cell connected to the closed circulating system. This fact suggests that bulk mass transfer effects to obtain the catalyst active sites were not important on the overall limiting kinetic rate.

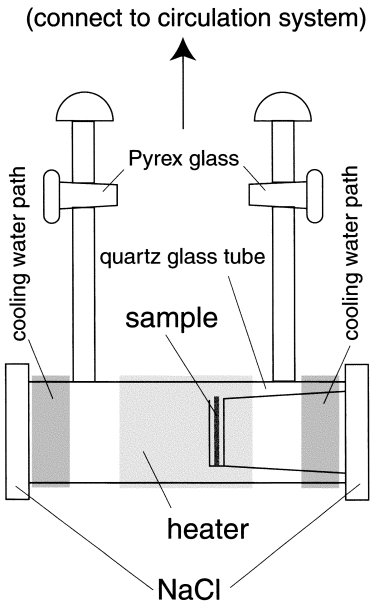


Fig. 1. In situ infrared sample cell.

Results

Kinetics. Twelve kinds of N_xO (x = 1, 2) removal reactions listed in the Experimental section were performed over Pd-H-ZSM-5 and conventional Pd/SiO_2 catalysts at 548 K. The steady-state rates are summarized in Table 1. For all the reactions (individual or simultaneous reactions and in the presence or absence of O_2 and propene), the rates were faster on Pd-H-ZSM-5 than on conventional Pd/SiO_2, even taking into account the difference of Pd loading of each catalyst (1.5 and 0.5 wt%, respectively). Namely, the rates on Pd-H-ZSM-5 were more than three times faster than those observed on Pd/SiO_2 in the corresponding reaction. H-ZSM-5 (Table 1) and SiO_2 were entirely inactive or showed smaller reactivity for NO removal at 548 K. NO reduction with propane or propene over H-ZSM-5 is reported at $\approx$673 K.[5] This result demonstrates that the Pd atom is the pertinent component of the active site for N_xO removal in these reaction conditions. The efficiency of Pd-H-ZSM-5 was reported for NO reduction with methane.[4,7,20] The acidity of zeolite was suggested to be an important factor in controlling the reaction rate.

For the reactions of N_xO and N_xO + O_2 (Table 1-i and ii), the rates of simultaneous reactions were almost the same as those for the individual reaction rates of N_2O. In the absence

Table 1. Steady-State N_2 Formation Rates (at 1 h Passed from the Beginning of Reaction; 10^{-6} mol h^{-1} g-cat^{-1}) from NO and/or N_2O over Pd-H-ZSM-5 and Supported Pd/SiO_2 Catalysts at 548 K

		Reaction Gas			
		(i)	(ii)	(iii)	(iv)
Catalyst	N_xO Type	N_xO	$N_xO + O_2$	$N_xO + C_3H_6$	$N_xO + O_2 + C_3H_6$
Pd-H-ZSM-5	NO	0.7	0.4	4.9	5.6(±0.1)
	N_2O	5.1	5.3	23	21(±1.2)
	$NO + N_2O$	5.0	5.0	28	34(±0.9)[a]
	$NO + N_2O + H_2O$[b]	—	—	—	28(±0.9)
Pd-Na-ZSM-5	NO	0.7	—	2.7	4.2
	N_2O	2.2	—	—	—
H-ZSM-5	NO	0	—	0	0
	N_2O	1.6	—	14	12
Pd/SiO_2	NO	0.2	—	0.4(±0.05)	0.5(±0.1)
	N_2O	0.5	—	1.7(±0.1)	2.5(±0.1)
	$NO + N_2O$	0.6	—	3.7(±0.2)	4.0(±0.1)
	$NO + N_2O + H_2O$[a]	—	—	—	3.1(±0.3)

The pressures of NO, N_2O, O_2, and propene were 0.56, 0.56, 8.1, and 0.56 kPa. The balance of the pressure to 101.3 kPa was made up with helium.
a) Corresponding to 2.7% conversion ($2[N_2]/([NO] + 2[N_2O])$. b) 0.56 kPa of water was also present.

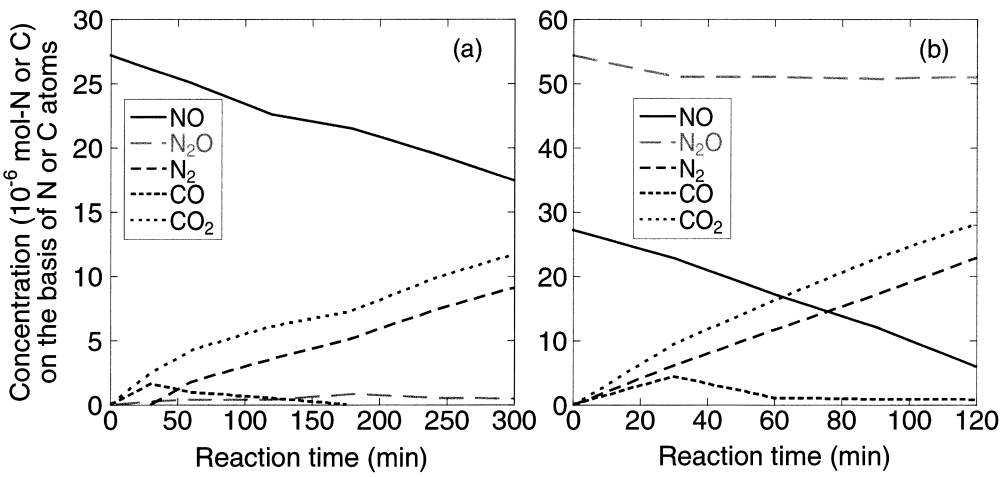


Fig. 2. The changes of concentration of reactants and products on the Pd-H-ZSM-5 catalyst for individual removal in NO + O_2 + propene (a) and for simultaneous removal in NO + N_2O + O_2 + propene (b). Reaction conditions are in footnote of Table 1.

of propene at 548 K, the reaction of N_2O to N_2 was so fast that the reaction of NO was negligible or the surface reaction site of NO was blocked by the presence of N_2O.

For the reaction of N_xO + propene (Table 1-iii), the reactions were dramatically promoted. All the reactions were promoted by the addition of propene, demonstrating that the N_2O reduction was also promoted by propene. The promotion of NO reduction by propene is well known. The major reaction route of propene should be the interaction with N_2O, based on the fact that the reaction in N_2O + propene was about five times faster than the reaction in NO + propene over both Pd-H-ZSM-5 and Pd/SiO_2 catalysts (Table 1). The rates of simultaneous reactions were the sum of the independent reactions of NO or N_2O for Pd-H-ZSM-5 and larger than the sum of the independent reactions for the conventional Pd/SiO_2 catalyst (76(±22)% enhancement). The error of enhancement ratio was based on the data deviations (Table 1) of individual removal rates for NO or N_2O and of simultaneous removal rate for NO + N_2O. The rate data deviations were estimated as the standard deviations when several reaction runs were performed in the same reaction conditions. Hence, in the presence of propene at 548 K, removal reactions of both NO and N_2O proceeded. The reaction of NO was not suppressed by the coexistence of N_2O for these Pd catalysts.

In the presence of O_2 and propene (Table 1-iv), reactions became rather faster than in the case in propene (Table 1-iii), except for the case of N_2O removal over Pd-H-ZSM-5. The reaction enhancement in the presence of O_2 was reported for the NO reduction by methane/propane over the Co-ZSM-5 catalysts.[2] The rates of simultaneous reactions were larger than the sum of the individual reactions for both Pd-H-ZSM-5 and Pd/SiO_2 catalysts (promotion ratio 28(±9) and 33(±12)%, respectively). The promotions of simultaneous removal contrast to the results of simultaneous removal on Co-ZSM-5 and Fe-MFI with hydrocarbon in the presence of O_2. The simultaneous removal rates were essentially the same as those ob-

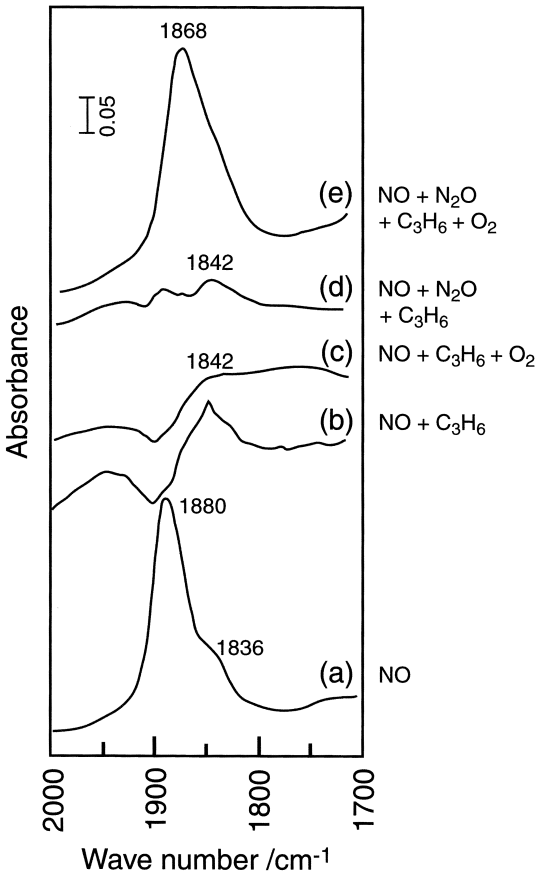


Fig. 3. In situ FT-IR spectra for Pd-H-ZSM-5 for 180 min at 548 K in various reaction conditions.

served for the individual removal rates of NO on Co-ZSM-5 and Fe-MFI.[2,3]

The effects of 0.56 kPa of water were tested for Pd-H-ZSM-5 and Pd/SiO_2 catalysts in NO + N_2O + O_2 + propene. ≈20% of activity loss was observed in the case of both catalysts (Table 1). The N_2 formation reactions over Pd-Na-ZSM-5 were always slower than those over Pd-H-ZSM-5 (Table 1).

The time courses of gas conversion on the basis of N and C atoms during the individual removal of NO and simultaneous removal in the presence of O_2 and propene on Pd-H-ZSM-5 are illustrated in Figs. 2a and b, respectively. As the concentration (reactants and products) was based on N or C atom, the concentration of N_2O (0.56 kPa) was twice as large as that of NO (0.56 kPa) at t (reaction time) = 0 in Fig. 2b. Figs. 2a and b show the time courses during 300 and 120 min, respectively. In Figure 2a (individual NO removal), ≈130% of CO_2 was formed compared to the degree of N_2 formation (C and N atom basis), but CO was produced in negligible quantities. Based on the detected products ratio at the steady state (after 60 min in Fig. 2), the reaction stoichiometry is simplified as $2NO + C_3H_6 + 7/2O_2 \rightarrow N_2 + 3CO_2 + 3H_2O$ (the CO_2: N of N_2 ratio is 150%). The hydrocarbon combustion $C_3H_6 + 9/2O_2 \rightarrow 3CO_2 + 3H_2O$ seems not to dominate the process. In Figure 2b (promoted simultaneous removal), the NO decrease and the N_2 increase were by about six times faster than in Fig. 2a. The N_2O decreased in the first 30 min, and remained (apparently) constant later. The formation ratios of CO and CO_2 to N_2 were similar to the case of Fig. 2a. The CO formation rates reached a maximum in the first 30 min and became negligible in 1–2 h in Figs. 2a and b. The reason may be that the oxygen atom adsorption on the Pd surface gradually increased and became constant within 1–2 h of the reaction being initiated, which is consistent with the decrease of N_2O (Fig. 2b) within first 30 min.

FT-IR Observations. The in situ FT-IR measurements were performed for Pd-H-ZSM-5 in NO, NO + propene, NO + O_2 + propene, NO + N_2O + propene, and NO + N_2O + O_2 + propene at 548 K. Spectra were measured at this temperature. Peaks were observed in the region of 2000–1700 cm^{-1} (Fig. 3). The wavenumbers of the peaks are summarized in Table 2, along with the reported values of NO adsorption.

An intense absorption peak was observed at 1880 cm^{-1} in NO and at 1868 cm^{-1} in NO + N_2O + O_2 + propene (Figs. 3a and e). A resolved shoulder peak also exists in NO at 1836 cm^{-1}, but the region was not well resolved in NO + N_2O + O_2 + propene. The intense peak in NO + N_2O + O_2 + propene was broader than that in NO, and was not symmetric, suggesting a weak feature on the lower-energy side.

The intense peak was not detected in NO + propene, in NO + O_2 + propene, or in NO + N_2O + propene (Figs. 3b– d). A medium-intensity peak was observed at 1842 cm^{-1} in NO + propene. The peak intensity became weaker or the peak disappeared by the addition of O_2 or N_2O. These peaks were not symmetric, suggesting an additional weak feature around 1870 cm^{-1}.

An intense, broad peak was observed at 2269–2251 cm^{-1} in NO + O_2 + propene and in NO + propene at 548 K for Pd-Na-ZSM-5 (not shown). Under these conditions, no peak was detected in this region for Pd-H-ZSM-5.

Two very broad peaks were also observed at 1730 and 1650 cm^{-1} in NO at 548 K for Pd-H-ZSM-5. The intensity was negligible, even when compared to weak peaks at 1842–1836 cm^{-1} (Fig. 3). The two broad peaks were also observed in NO at 548 K for conventional Pd/SiO_2 catalyst. The FT-IR spectrum for conventional Pd/SiO_2 was essentially the same as those in Refs. 12 and 13.

Discussion

FT-IR Peak Assignments. The infrared absorption measurements were performed at 548 K, and three kinds of peaks (1880, 1868 and 1842–1836 cm^{-1}) were observed (Table 2 and Fig. 3). The NO adsorption peak on H-ZSM-5 was observed at 1877 cm^{-1}, which is almost the same wavenumber as for free NO: 1876 cm^{-1}. However, the intensity was only a few percent compared to the peak due to NO adsorption on Pd-H-ZSM-5. The N_2O adsorption was not observed on Pd-H-ZSM-5 in the detection limit of FT-IR.[16] Hence, the observed peaks should be due to adsorbed NO. It is also possible for them to be intermediate species of the reaction route starting from NO and terminating with N_2, because the FT-IR measurements were performed at 548 K. However, the adsorption peaks due to NCO,[21] NO_2,[10,11] or N_2[18] in the region of 1920–1800 cm^{-1} are not reported, or the adsorbed species have already desorbed at 548 K. The intense, broad peak at 2269–2251 cm^{-1} observed on Pd-Na-ZSM-5 can be assigned to NCO.[21]

The adsorption of NO on reduced metallic particles on a Pd/

Table 2. Observed Absorption Peak Wavenumbers (cm^{-1}) in the FT-IR Spectra for Pd-H-ZSM-5- in Various Reactions at 548 K (a) and Reported Values of NO Adsorption Wavenumbers (cm^{-1}) (b)

(a)

Catalyst	NO	NO + propene	NO + O_2 + propene	NO + N_2O + propene	NO + N_2O + O_2 + propene
Pd-H-ZSM-5	1880 (s), 1836 (m, sh)	1842 (m)	1842 (w, br)	1842 (m, br)	1868 (s) 2994 (w) 2937 (w) 2903 (w)
Blank	1876				

The pressure of the gas was the same as in Table 1.

(b)

Catalyst	NO	Reference
Pd/SiO_2	1660–1645, 1750–1730	12, 13
Pd-ZSM-5	1881, 1836 (NO)	10
Cu-ZSM-5	1827, 1734 (twin $(NO)_2^{\delta-}$), 1813 ($NO^{\delta-}$), 1906 ($NO^{\delta+}$), 1964 (Cu_n–$NO^{\delta+}$)	22
Fe-Y[a)]	1918, 1815 (twin NO) 1882, 1850, 1760 (NO)	23

a) Similar peak pattern was observed also for Fe-mordenite and Fe-ZSM-5.

SiO_2 surface was reported at 1660–1645 and 1750–1730 cm^{-1} (Table 2).[12,13] They were assigned as linear or bridged NO on the Pd particles. Particle size effects on the NO stretching wavenumber are known. The NO stretching wavenumber increases as the coverage of NO increases, due to the dipole–dipole interactions.[13] However, even when the particle size effects and the dipole–dipole coupling effects are taken into account, the wavenumbers of peaks in Fig. 3 are larger by more than 100 cm^{-1} compared to reported peaks on metallic Pd. This difference demonstrates that the observed NO peaks (1880, 1868 and 1842–1836 cm^{-1}) were ascribed to NO on isolated Pd cations inside the zeolite cage and that broad, very weak peaks at 1730 and 1650 cm^{-1} were due to NO on metallic Pd particle under our reaction conditions.

As examples of NO adsorption on metal cations inside zeolites, the absorption peak values are listed in Table 2b for Pd-ZSM-5,[10] Cu-ZSM-5[22] and Fe-ZSM-5, Fe-Y, and Fe-mordenite.[23] The peak energy splitting of symmetric and asymmetric peaks of twin NO species was 93–103 cm^{-1}. Looking at the splitting between peaks in Fig. 3, which is 26–44 cm^{-1}, we do not assign them to twin NO species. In fact, their intensities did not follow the same trend in the time course of measurements of the catalytic reaction or of the gradual gas-phase evacuation. For the mononitrosyl species, the adsorption peak energy varied by 93–151 cm^{-1} for Cu-ZSM-5 and 32–122 cm^{-1} for Fe-Y (Fe-ZSM-5) due to the difference of charge on the nitrosyl group. Therefore, the peaks at 1880, 1868, and 1842–1836 cm^{-1} can be assigned as mononitrosyl $NO^{\delta+}$, $NO^{\pm0}$, and $NO^{\delta-}$, respectively, on the Pd cation. Rather than other species (N_2O, propene, or O_2) directly affecting the wavenumber of nitrosyl on Pd (change from Figs. 3a to b–d), these other species may preferentially block adsorption sites for $NO^{\delta+}$ or $NO^{\pm0}$. The charge on the nitrosyl group is based on each wavenumber compared to the free NO (1876 cm^{-1}). Whether the 4*d* orbital of the Pd cation back-donates charge to the NO π^* orbital or whether the filled NO σ orbital donates a charge to the unfilled Pd 4*d* orbital, the $\nu_{N\text{-}O}$ stretching wavenumber will decrease or increase, respectively, compared to the free value of 1876 cm^{-1}.[24]

The peak at 1842 cm^{-1} appears in the presence of propene, and can be assigned as bridging or multifold CO on the Pd instead. As no corresponding peak of terminal CO on Pd was detected within the range 2100–1900 cm^{-1} and CO formation in 3 h of the reactions NO + propene + O_2 or NO + N_2O + propene at 548 K was negligible (Fig. 2), the possibility of the 1842 cm^{-1}-peak assignment being due to CO seems small. The peaks observed at 1881 and 1836 cm^{-1} on oxidized 0.5 wt% Pd-ZSM-5 at 300 K were assigned to mononitrosyl on Pd^{I} ligated by lattice oxygen atoms and to mononitrosyl on Pd^{I}, where one of the O ligands was replaced by a water molecule, respectively.[10] In the cases shown in Figs. 3b–e, it is possible that the water molecule of the reaction product ligated to the Pd ion.

In the presence of O_2, an additional peak at 2133–2125 cm^{-1} has been reported, and this was assigned as NO_2^+ (Cu-MFI-81),[22] NO_2 (Pd-H-ZSM-5),[10] or NO^+ (Pd-H-ZSM-5).[11] No peaks were observed in this wavenumber region for Pd-H-ZSM-5 and Pd-Na-ZSM-5 in in situ reaction condition in this study. This comparison is not contradictory because the peak at 2133 cm^{-1} completely desorbed at 373 K,[11] whereas our measurement temperature of FT-IR was 548 K.

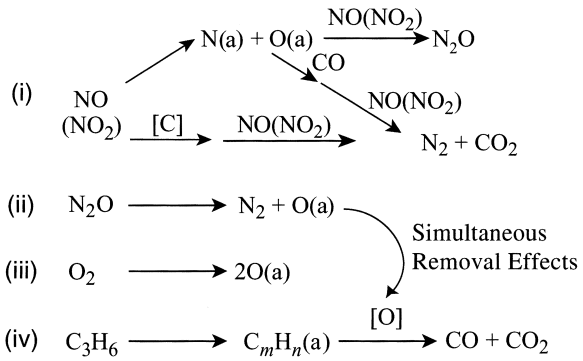
The N_xO removal was enhanced by the coexistence of NO and N_2O in the case of reactions of NO + N_2O + O_2 + propene on Pd-H-ZSM-5 when compared to the sum of the individual removal rates in the corresponding conditions (Table 1). The reactions were monitored by in situ FT-IR. The intense

peak of mononitrosyl $NO^{\pm 0}$ was observed with similar peak intensity to the NO adsorption (Figs. 3e and a), suggesting the importance of mononitrosyl $NO^{\pm 0}$ in catalysis. In the absence of N_2O in the reaction mixture, only the very weak peak of mononitrosyl $NO^{\delta-}$ (*or* weak CO) was observed in NO + O_2 + propene (Fig. 3c).

In the absence of O_2, the simultaneous removal rate of NO + N_2O was the sum of the individual removal rates of NO and N_2O on Pd-H-ZSM-5 (Table 1). Only the peak due to mononitrosyl $NO^{\delta-}$ (*or* weak CO) was observed both in NO + propene and in NO + N_2O + propene (Figs. 3b and d).

Reaction Mechanism. One of the possible effects of propene is to offer carbon in the reaction route via NCO.[5,21] The activation of propene is believed to be related to the acidity of the zeolite.[4,20] The effects of acidity were implied in the comparison of the activity between Pd-H-ZSM-5 and Pd-Na-ZSM-5 (Table 1). The N_2 formation rates were always higher over more acidic Pd-H-ZSM-5 than over less acidic Pd-Na-ZSM-5. Compared to the gas-phase propene molecules (ν_{CH} = 2991.5, 2932.7, and 2869.8 cm^{-1}),[25] three weak peaks at 2994, 2937, and 2903 cm^{-1}) were observed for Pd-H-ZSM-5 in NO + N_2O + O_2 + propene at 548 K (Table 2). As these three peaks should be typical vibration peaks of CH_2 and CH_3, surface carbonaceous species were proposed to exist during catalysis. Surface carbonaceous species derived from propene react with adsorbed NO (*or* NO_2 in the presence of O_2),[3,6] or adsorbed CO reacts with nitrogen species, and further reacts with another NO molecule (*or* NO_2 in the presence of O_2) to form N_2 + CO_2 or N_2O (Scheme 1-i). [5,21] The carbonaceous species can be consumed to form CO and CO_2 in the route of by-reaction (Scheme 1-iv) or can remain as surface deposits that act as an inhibitor of catalysis. It is unclear why the NCO species was detected on Pd-Na-ZSM-5 and *not* on Pd-H-ZSM-5 in NO + propene or in NO + O_2 + propene at 548 K. The N_2 formation rates on the former were slower (55–75%) than those of the latter. The NCO on the Pd of the former catalyst may poison the site, but NCO did not adsorb on the latter catalyst in the time scale of the FT-IR measurements (i.e. stayed on the surface during a very short time), and may convert quickly to N_2.

We propose that the key to the promotion of simultaneous removal on Pd-H-ZSM-5 is the dissociated oxygen atom of the adsorbed N_2O (Scheme 1-ii). The oxygen atom separated from N_2O on the catalyst surface may play a role in controlling the



Scheme 1. Proposed reaction pathway of the promoted simultaneous catalytic removal of NO and N_2O in the presence of O_2 and propene.

appropriate concentration of surface carbonaceous species to below the level that leads to inhibition of NO adsorption and dissociation (Scheme 1). The importance of carbonaceous species produced from NO + hydrocarbon has been suggested elsewhere.[3,6,26,27] The effects of oxygen derived from N_2O may be similar to the effects of the oxygen derived from O_2 or NO (Scheme 1),[2] but the dissociation of N_2–O is thermodynamically far easier than that of O–O or N–O. N_2O decomposition is reported to be insensitive to the presence of O_2, whereas NO decomposition is often influenced by the presence of O_2.[2,4,6,8,9,11,20,28] This general trend may suggest different active sites for NO and N_2O dissociation. An alternative interpretation is that the reactivity of NO and N_2O is different with metal ion in zeolite, and dissociated oxygen species may have different chemical natures. More reactive oxygen species dissociated from N_2O were reported on Cu-ZSM-5 (Cu^{2+}-O^-)[28] and on Fe-ZSM-5 (α-oxygen).[29] Rate dependence on reactant pressure should be monitored to make this effect of O of N_2O more certain. The N_2O concentration was constant in Fig. 2b after 30 min of reaction, due to the steady-state balance of N_2O decomposition and the formation from NO. With the major effects of dissociated oxygen derived from N_2O to remove the carbonaceous species on surface Pd cation, the $NO^{\pm 0}$ on the Pd cation (1868 cm^{-1}) became the major surface species (Fig. 3e). As the concentration of this species is the balance of the reaction path rates in Scheme 1, the promotion effects were not observed in NO + N_2O + propene (in the absence of O_2) on Pd-H-ZSM-5.

The surface site of the 1868 cm^{-1}-peak is suggested to be responsible for the dissociation of NO (Scheme 1-i) in the promoted simultaneous removal. Aparicio et al. reported the correlation between the N_2O decomposition reaction and the mononitrosyl IR peak intensity, and suggested that the mononitrosyl site is the active site for Fe-ZSM-5.[23] The Pd ion introduced to H-ZSM-5 (0.3 wt% of Pd) was reported to exist as Pd^{2+} in the reaction condition of the NO + CH_4 + O_2 reaction at 773 K, based on the X-ray absorption fine structure spectroscopy.[7] The Pd ion introduced to H-ZSM-5 (0.44 wt% of Pd) existed as Pd^{2+} below 610 K and is suggested to be the active site for NO reduction by methane, based on the FT-IR measurements.[11] As the pertinent Pd sites for NO and/or N_2O decompositions were found to be dispersed Pd^{2+} inside zeolite (Pd-H-ZSM-5) and small Pd particles (Pd/SiO_2) in this paper, the reaction mechanism of NO and/or N_2O decompositions should be different.

The intensity of two very broad peaks (1730 and 1650 cm^{-1}) in NO at 548 K for Pd-H-ZSM-5 that could be ascribed to mononitrosyl on Pd particles was negligible. Either only a small amount of Pd particles existed, or the surface of the Pd metal particles was dominantly covered by oxygen (similar effects were reported in Ref. 11) such that it could not adsorb NO in the reaction conditions used for NO and/or N_2O removal. Either possibility supports Pd^{2+} sites inside zeolite to be active sites in the case of Pd-H-ZSM-5 catalyst.

The *promoted* simultaneous removal was observed for Pd/SiO_2 but not for Pd-H-ZSM-5 in the presence of propene and absence of O_2 (Table 1-iii). One of the possible reasons of this difference is the different dissociation ability of N_2–O bond either in the case of Pd microparticle (Pd/SiO_2) or Pd ion (Pd-H-

ZSM-5). The steady-state formation rate of $N_2 + 1/2O_2$ from N_2O was as much as ≈10 times faster on Pd-H-ZSM-5 than on Pd/SiO_2 (Table 1-i), but the initial non-stoichiometric N_2 formation was faster on Pd/SiO_2 rather than on Pd-H-ZSM-5. Therefore, the dissociation of N_2–O bond was faster on Pd microparticle surface than on Pd ion site, but the formation and desorption of O_2 was slow on Pd microparticles. In the presence of propene, formed surface O species can be converted by carbonaceous species derived from propene. N_2–O bond dissociation (Scheme 1-ii) was fast enough on Pd/SiO_2, and the promoting effect of O(ad) (i.e. promoted simultaneous removal) for the reaction step (iv) of Scheme 1 may be observed in the presence of propene only for Pd/SiO_2.

The biggest question still remains; why simultaneous removal was promoted via the oxygen atom dissociated from N_2O only on the Pd ion and not on the Co and Fe ions.[2,3] As H-ZSM-5 was inactive for NO removal in the reaction conditions in this paper, the difference may be ascribed to the difference of valence state among metals. These metal-zeolite catalysts were prepared from Pd^{2+}, Co^{2+}, and Fe^{2+}.[2,3] As exchanged Co^{2+} and Fe^{2+} can be oxidized to Co^{3+} and Fe^{3+}, dissociated O may be bound to Co^{3+} or Fe^{3+} and stabilized. On the other hand, the redox of palladium is between Pd^0 and Pd^{2+} and dissociated O may be unstable when it is bound to Pd^{2+}. These difference of valence states among metals may be the major reason that promoted simultaneous removal of NO + N_2O was observed only in the case of Pd catalysts. The oxygen atom dissociated from N_2O may be relatively unstable on the Pd site, and further reaction with carbonaceous species formed from propene can occur very quickly.

Conclusions

1. Simultaneous removal of NO + N_2O was promoted in O_2 + propene over Pd-H-ZSM-5 and conventional Pd/SiO_2 catalysts, and in propene on conventional Pd/SiO_2, when compared to the sum of the corresponding individual removal rates of NO or N_2O.

2. In the conditions that promoted simultaneous removal, an intense peak ascribed to the $NO^{\pm 0}$ on Pd cation in a ZSM-5 cage was observed at 1868 cm^{-1}. When NO was introduced to Pd-ZSM-5, the mononitrosyl ($NO^{\delta+}$) peak was observed at 1880 cm^{-1}. In the other conditions used for individual removal or unpromoted simultaneous removal, a medium or weak peak was observed at 1842 cm^{-1}.

3. Based on peak intensity in FT-IR spectra, the pertinent state of palladium for NO and/or N_2O decomposition was found to be Pd^{2+} for Pd-H-ZSM-5, in contrast to the two broad peaks ascribed to surface metal particles observed for conventional Pd/SiO_2.

4. The promotion effects of the oxygen atom dissociated from N_2O were suggested as a mechanism for keeping the Pd site clear from extra carbonaceous species. The relative stability of the oxygen may be related to the difference between promoted simultaneous removal on the Pd site and essentially the same rates of simultaneous removal as NO removal (N_2O removal was inhibited) on the Co and Fe sites.

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