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MnO_x−CeO_2 Binary Oxides for Catalytic NO_x-Sorption at Low Temperatures. Selective Reduction of Sorbed NO_x

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The reactivity of NO_x sorbed onto MnO_x−CeO_2 toward H_2 was studied in the presence of impregnated Pd catalyst by use of TPR, H_2 pulse reactions, in situ FT-IR, and steady-state NO−H_2−O_2 reactions. The Pd-loaded catalyst after saturated NO_x-sorption at 150 °C could be regenerated by micropulse injections of H_2, which ensure the reduction of monodentate, bidentate, and ionic nitrates sorbed on MnO_x−CeO_2 into N_2. In the steady-state NO−H_2−O_2 reaction, gaseous NO_x was first sorbed onto MnO_x−CeO_2 and subsequently reduced at the PdO/MnO_x−CeO_2 boundary. Despite the nonselective character of Pd catalysts toward NO_x−H_2 reaction, Pd/MnO_x−CeO_2 attained 65% NO-conversion of a stream of 0.08 vol % NO, 2 vol % H_2, and 6 vol % O_2 in He at a low temperature of 150 °C, compared to ~30% for Pd/γ-Al_2O_3, the reaction on which was more suppressed by the competitive H_2−O_2 reaction. The combination of NO_x sorbability of MnO_x−CeO_2 and H_2 activation of Pd catalysts was found to give rise to a synergistic effect, thus paving the way to development of NO_x-sorbing catalysts for selective deNO_x processes at low temperatures (<150 °C).

Introduction

Sorptive removal has become an interesting approach to NO_x control in a strongly oxidizing atmosphere, where conventional catalytic reduction with H_2 and/or CO is strongly inhibited by coexisting excess oxygen.[1,2] Several researchers have already studied the sorptive NO_x removal by use of alkaline solids,[3] metal oxides,[4−13] and microporous materials.[14,15] We have first studied solid−gas reactions between various Ba cuprates and NO, which lead to the precipitation of barium nitrate or nitrite.[6,16] The regeneration of NO_x-sorbents in such systems can be achieved simply by heating to decompose the nitrate/nitrite at >600 °C, and thus, sorption/desorption can be repeated by applying temperature-swing cycles.[17] In a parent paper,[18] we reported sorption/desorption properties of NO_x over MnO_x−CeO_2 solid solutions with the fluorite-type structure. The oxides possess the combination of NO_x-oxidation activity and moderate basicity, yielding significant synergism in the oxidative adsorption as monodentate, bidentate, and ionic nitrates at ≤150 °C. Unlike the Ba-containing sorbents, MnO_x−CeO_2 can liberate the sorbed NO_x at relatively low temperatures of 300−350 °C, so that the high reactivity to reducing agents is expected to establish an alternative process to regenerate the sorbents. In particular, NO_x-sorbing catalysts, which enable conversion of significant amounts of stored NO_x to N_2, are of strong interest. A process alternating NO_x-sorption and subsequent reduction can be seen in the so-called "NO_x storage and reduction catalysts", which have been developed by Toyota.[19] In the catalyst system under oxidizing atmosphere, NO_x is stored into an alkali component dispersed on the catalyst surface. This is followed by supplying short periods of reducing gas during which the resultant exotherm leads to thermal desorption of NO_x and subsequent reduction to N_2 on noble metal catalysts. Unfortunately, however, none of such catalysts reported so far can be used in a steady-state gas flow at <150 °C.

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Our concept for the NO_x-sorbing catalysts in the present study is to bring about sorptive removal of NO_x and its simultaneous catalytic reduction at the lowest possible temperatures in the presence of excess O_2. With the use of noble metals, it is expected to not only activate reducing agents but also promote the reaction with stored NO_x to N_2 with a minimum hindrance effect from coexisting gaseous O_2. In the first step of this concept, the aim of the present study is to obtain information upon the reactivity of nitrate sorbates formed on MnO_x-CeO_2 when they are exposed to H_2 in an oxidizing atmosphere. For this purpose, we have employed Pd as a hydrogen-activating catalyst, which is known not to be selective to $NO-H_2$ reactions due to a competitive H_2-O_2 reaction. The reaction between H_2 and stored NO_x was studied by TPR, pulse reactions, and steady-state $NO-H_2-O_2$ reactions, and the results are correlated with those obtained by FT-IR, XRD, and XPS.

Experimental Section

Preparation and Characterization. The equimolar binary oxide, MnO_x-CeO_2, was prepared by coprecipitation from aqueous solutions of nitrates. Calculated amounts of $Mn(NO_3)_2·6H_2O$ and $Ce(NO_3)_3·6H_2O$ (Wako Chemicals, Guaranteed reagent grade) were dissolved in distilled water. Addition of an aqueous ammonia solution dropwise to the solution produced precipitates, which were evaporated to dryness and subsequently calcined at 450 °C for 5 h in air. An aqueous solution of $Pd(NO_3)_2$ was impregnated onto as-prepared oxides and calcined at 450 °C for 5 h to produce Pd-loaded samples (0.1, 0.5, and 1.0 wt % loading as Pd). As-prepared powder samples were pressed and crushed into 20 mesh granules before use.

Crystal structures of calcined samples were determined by powder X-ray diffraction (XRD, Shimadzu XD-D1) using monochromated Cu Kα radiation (30 kV, 30 mA). The BET surface area was obtained by measuring N_2 adsorption isotherms at −196 °C. The XPS measurement was performed on a Shimadzu-Kratos AXIS-HS spectrometer with a magnesium anode (Mg Kα, 1253.6 eV) operated at 15 kV and 10 mA. The binding energy calibration was checked by the line position of C 1s as an internal reference (284.6 eV). The normal operating pressure in the analysis chamber was controlled to less than 10^{-6} Pa during the measurement.

In Situ FT-IR. FT-IR spectra of NO_x species adsorbed on Pd/MnO_x-CeO_2 were recorded on a Jasco FT-IR610 spectrometer. A temperature-controllable diffuse reflectance reaction cell (Jasco DR600A) was connected to a gas flow system and a vacuum line. The sample was first outgassed in a stream of 20 vol % O_2/He at 400 °C for 1 h and then exposed to the reaction gases containing 0.08 vol % NO, 2 vol % O_2, and He balance at 150 °C for 30 min. This was followed by treatment at 150 °C for 30 min in flowing 10 vol % H_2/He and, subsequently, a second NO_x-sorption at 150 °C. After each treatment spectra were recorded in flowing He at ambient temperature.

TPR. The reactivity of sorbed NO_x to H_2 was characterized by means of temperature-programmed reduction (TPR) in a conventional flow reactor connected to a volumetric vacuum system and to a differential evacuation system. Prior to the measurement, the sample (0.2 g) was submitted to NO_x-sorption (0.08 vol % NO, 2 vol % O_2, balanced with He) at 150 °C for 30 min. After subsequent evacuation at ambient temperature, the sample was heated in a flowing gas mixture of 5 vol % H_2 in He (20 cm^3/min) at a constant rate (10 °C/min). Gas mixtures desorbed from the sample were analyzed by a quadrupole residual gas analyzer mass spectrometer (LEDA-MASS, MoniTorr).

H_2 Pulse Injection during NO_x-Sorption. The reactivity of sorbed NO_x to H_2 was also evaluated in pulse mode reactions. The sample (0.2 g) was placed in a stream of NO_x (0.08% NO, 2 vol % O_2 balanced with He, W/F = 0.24 s·g/cm^3) at 150 °C. After the effluent NO_x increased toward the saturation of sorption, 1 cm^3 of H_2 was injected into the stream just before the catalyst bed every 10−20 min. NO_x (NO/NO_2) and other gas species in the effluent were monitored by using a chemiluminescence NO_x analyzer (Shimadzu NOA-305) and a mass spectrometer, respectively.

Table 1. BET Surface Area and NO_x Uptake

	surface area/m^2g^{-1}	NO_x uptake^a/mmol·g^{-1} 30 °C	NO_x uptake^a/mmol·g^{-1} 150 °C
MnO_x-CeO_2	64.2	0.17	0.11
1 wt % Pd/MnO_x-CeO_2	77.8	0.27	0.15
γ-Al_2O_3	186	-	0.01
1 wt % Pd/γ-Al_2O_3	180	-	0.11

[a] 0.08 vol % NO, 2 vol % O_2, He balance, W/F = 0.24 g·s/cm^3.

Steady-State $NO-H_2-O_2$ Reactions. The steady-state $NO-H_2-O_2$ reactions were carried out in a conventional flow system at atmospheric pressure. The sample (0.2 g) was fixed in a quartz tube (4 mm i.d.) by packing quartz wool at both ends of the bed. Gaseous mixtures of 0.08−0.2 vol % NO, 0−4 vol % H_2, and 0−10 vol % O_2 in He were fed to the sample at W/F = 0.24 g·s/cm^3. The reactor effluent was analyzed by on-line gas chromatography (GL Science Model 370) with molecular sieve 5A and Porapak-Q columns and a chemiluminescence NO_x analyzer.

Results and Discussion

Structure and NO_x Uptake of Pd/MnO_x-CeO_2. In the preceding paper,[18] we reported the results of characterization for the binary oxides, $(n)MnO_x-(1-n)CeO_2$ by use of XRD, XPS, TPD, and FT-IR. The oxides with the composition $n \leq 0.5$ are composed of a fluorite-type solid solution. Owing to the redox property of Mn in the lattice, the solid solution is effective in promoting oxidative sorption of NO as nitrates. As in the case of unloaded samples, 1 wt % Pd/MnO_x-CeO_2 exhibited broad X-ray diffraction peaks ascribable only to fluorite, but peaks corresponding to Pd phases were too weak to be observed because of the small amount and low crystallinity. The XPS measurement in the Pd $3d_{5/2}$ region consisted of a single component at $E_B = 336.8$ eV, demonstrating that the surface Pd species are in the form of oxide (PdO). Since the Mn 2p signals were not affected by impregnating Pd, it seems to be mainly in the trivalent state (Mn^{3+}), as it was in the unloaded sample.[18] Table 1 shows the effect of Pd loading on BET surface area and NO_x uptake of MnO_x-CeO_2. Clearly, impregnating Pd catalysts increased the NO_x uptake irrespective of temperatures. Figure 1 compares the FT-IR spectra for the Pd-loaded and unloaded MnO_x-CeO_2 after NO_x uptake at 150 °C. Both the samples showed bands due to ionic nitrate (1320 and 1030 cm^{-1}) and monodentate and bidentate nitrates (1625, 1545, 1445, and 1375 cm^{-1}), covalently bonded to the surface cerium ions. These spectra are consistent with the oxidation of NO to NO_2 followed by coordination to a $Ce^{4+}-O^{2-}$ pair to produce covalent nitrates and further conversion to ionic nitrates.[18] By loading Pd catalysts, the ionic nitrate bands were found to become intense relative to the covalent nitrate bands. The oxidative adsorption as ionic nitrates was also enhanced when the adsorption onto unloaded MnO_x-CeO_2 was carried out with incremental O_2 pressures or at higher temperatures. Therefore, it is assumed that the Pd oxides accelerate oxidation of NO to NO_2 and resultant formation of ionic nitrates on

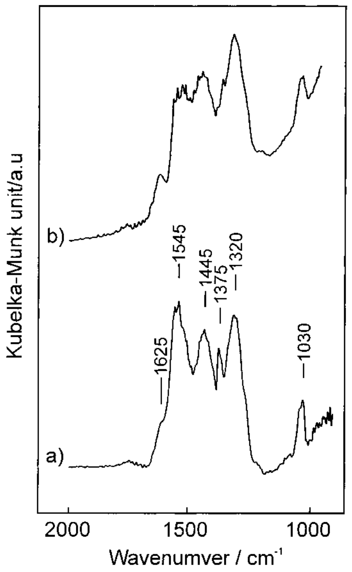

Figure 1. FT-IR spectra of (a) MnO_x-CeO_2 and (b) 1 wt % Pd/MnO_x-CeO_2 after exposure to 0.08 vol % NO, 2 vol % O_2/He at 150 °C.

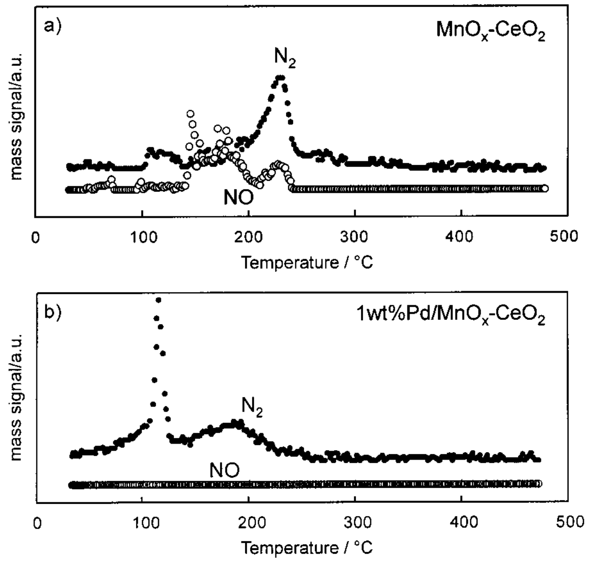

Figure 2. Gas evolution from (a) MnO_x-CeO_2 and (b) 1 wt % Pd/MnO_x-CeO_2 during TPR in flowing gas mixtures of 5 vol % H_2 in He.

MnO_x-CeO_2. The effect of Pd could also be confirmed by the comparative measurement on γ-Al_2O_3 (Table 1); NO_x uptake was negligible for γ-Al_2O_3 alone in contrast to Pd/γ-Al_2O_3.

Reactivity of Sorbed NO_x to H_2. To evaluate the reactivity of the nitrate sorbates in a reducing atmosphere, NO_x-sorbed samples were heated at a constant rate at 10 °C/min in a stream of 5 vol % H_2/He. Besides water elimination, N_2 and NO could be detected as N-containing compounds at different temperatures. Figure 2 shows the resulting gas evolution profiles from MnO_x-CeO_2 and 1 wt % Pd/MnO_x-CeO_2 as a function of heating temperature. The unloaded sample after an NO_x uptake of 0.11 mmol/g at 150 °C displayed several NO peaks at 150−250 °C and a N_2 peak at 230 °C. According to our previous paper,[18] the TPD measurement of NO_x-sorbed samples showed the two desorption peaks of NO/NO_2 at 200 and 290 °C, which are attributed to covalent and ionic nitrate adsorbates, respectively. In comparison, the desorption in Figure 2a was completed at <250 °C, probably because of the instability of nitrate adsorbates in a reducing atmosphere. The following evolution of N_2 at ~230 °C was produced by reduction of nitrate sorbates. Introducing H_2/He mixtures into the Pd-loaded sample at ambient temperature produced a much larger amount of water as a result of the reduction of PdO. But, more noticeable is that the sorbed NO_x (0.15 mmol/g) in this case led to two N_2 peaks at 120 and 190 °C without eliminating detectable NO_x up to 470 °C. Thus, NO_x sorbed onto MnO_x-CeO_2 could be almost completely reduced to N_2 in the presence of the Pd catalyst.

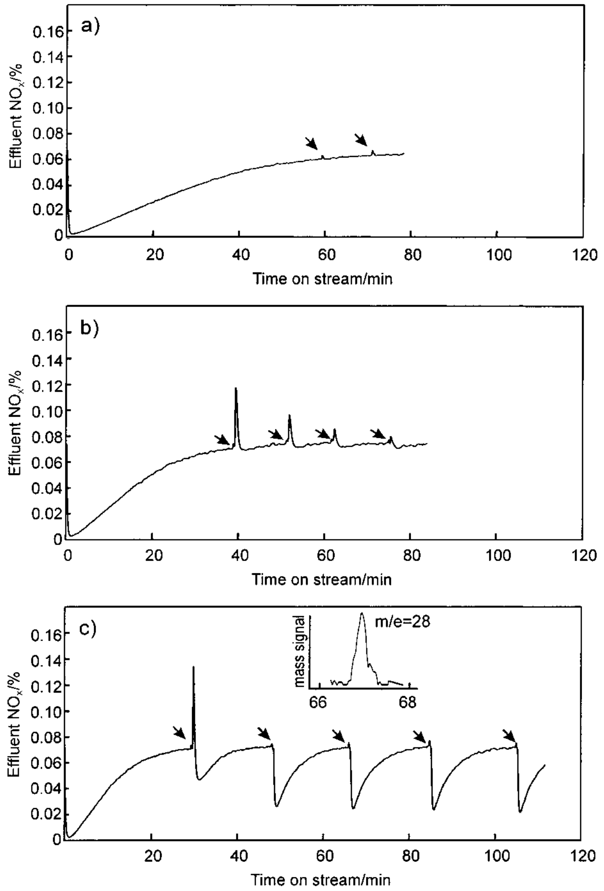

Figure 3. Effect of H_2 pulses on the effluent NO_x from 1 wt % Pd/MnO_x-CeO_2 at (a) 30 °C, (b) 100 °C, and (c) 150 °C. Each H_2 pulse was 1.0 cm^3. Gas feed: 0.08 vol % NO, 2 vol % O_2, He balance, $W/F = 0.24$ g·s/cm^3.

The reduction of sorbed NO_x was also examined by the method of micropulse injection of H_2. In this measurement, 1 wt % Pd/MnO_x-CeO_2 was placed in a flowing gas mixture (0.08 vol % NO, 2 vol % O_2, and He balance) with monitoring NO_x concentration in the reactor effluent, as shown in Figure 3. On approaching the saturation of sorption, the injection of 1 cm^3 of H_2 into the gas feed was repeated (shown as arrows in the figure). In all case in Figure 3, the incremental concentration from the beginning of the reaction corresponds to a breakthrough curve of NO_x-sorption. The sorptive NO_x removal at 30 °C lasted over 60 min without being affected by H_2 pulses (a). At 100 °C, the H_2 pulse immediately generated sharp but small evolutions of NO_x (b). The oxidation of H_2 over Pd oxide would create a local exotherm, and the resulting temperature rise would promote desorption of NO_x species adsorbed

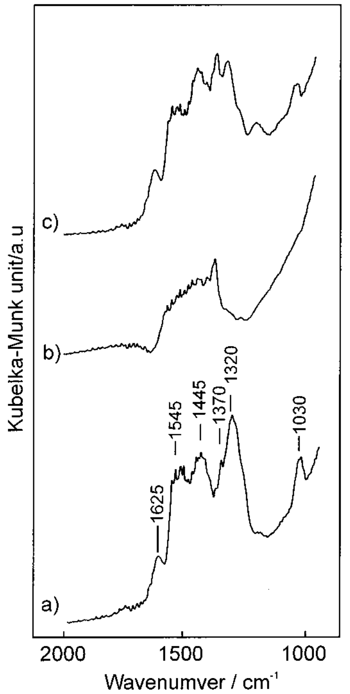

Figure 4. FT-IR spectra of 1 wt % Pd/MnO_x−CeO_2 after (a) exposure to 0.08 vol % NO, 2 vol % O_2/He at 150 °C and subsequent exposure to (b) 10 vol % H_2/He at 150 °C and then (c) 0.08 vol % NO, 2 vol % O_2/He at 150 °C.

thereon. However, the peak decreased in intensity with repeating H_2 pulse injections. The most remarkable response was observed at 150 °C (c); that is, the first injection of 1 cm^3 of H_2 immediately gave a sharp NO_x-desorption followed by a steep drop of the NO_x concentration, accompanied by the evolution of N_2, as evident from parallel mass spectra measurements. The NO_x concentration was then increased slowly again, as was observed before the first H_2 pulse. As judged from the apparent thermal desorption of NO_x, it seems that part of the H_2 in the first injection reacted with PdO, whereas those after the second injection were consumed mainly to reduce nitrate adsorbates, causing a larger extent of regenerative capacity for NO_x-sorption. The regenerative capacity of NO_x-sorption increased with a number of the H_2 pulses and finally exceeded 50% of the maximum uptake (0.15 mmol/g). Assuming the stoichiometric reaction, $2NO_2 + 4H_2 \rightarrow N_2 + 4H_2O$, this corresponds to ~70% selectivity of H_2 in every injection to the reduction of NO_x stored.

To clarify the change of nitrate sorbates in the reducing atmosphere, in situ FT-IR measurement was used (Figure 4). When NO_x-sorbed 1 wt % Pd/MnO_x−CeO_2 was placed in a flowing mixture of 10 vol % H_2/He at 150 °C for 10 min. The ionic nitrate bands (1320, 1030 cm^{-1}) disappeared, leaving the very weak bands of monodentate and bidentate nitrates (b). However, the bands of nitrates were restored after subsequent exposure to a stream of NO_x mixtures (0.08 vol % NO and 2 vol % O_2 and He balance) at 150 °C (c). These results suggest that the nitrate formed on MnO_x−CeO_2 can be removed as N_2 by the reaction with H_2 in the presence of impregnated Pd catalysts.

The H_2 pulse injection during NO_x-sorption was also applied to two reference compounds, MnO_x−CeO_2 and 1 wt % Pd/γ-Al_2O_3, as shown in Figure 5. When the neat MnO_x−CeO_2 sample was used (a), the NO_x breakthrough curve was not influenced by the repeated injection of H_2 pulses, reaching toward saturation after ~40 min rof eaction time without a detectable drop of the effluent NO_x concentration. On the other hand, Pd/γ-Al_2O_3 exhibited responses clearly but quite differently from those in Figure 3c. The regenerative capacity of NO_x-sorption upon each H_2 pulse was less than 20% of that shown in Table 1 and decreased with the number of pulsing. Moreover, a large NO_x-desorption observed after every injection of H_2 suggested a dominant H_2−O_2 reaction over Pd catalysts and a resultant significant temperature rise. These results support data by TPR and FT-IR, indicating that the combination of two components, Pd and MnO_x−CeO_2, is essential to ensure the reaction between hydrogen and nitrate adsorbates. Since H_2 cannot be activated on MnO_x−CeO_2 at low temperatures, the reaction would take place in the vicinity of the boundary with PdO, where both hydrogen and nitrate must be abundant.

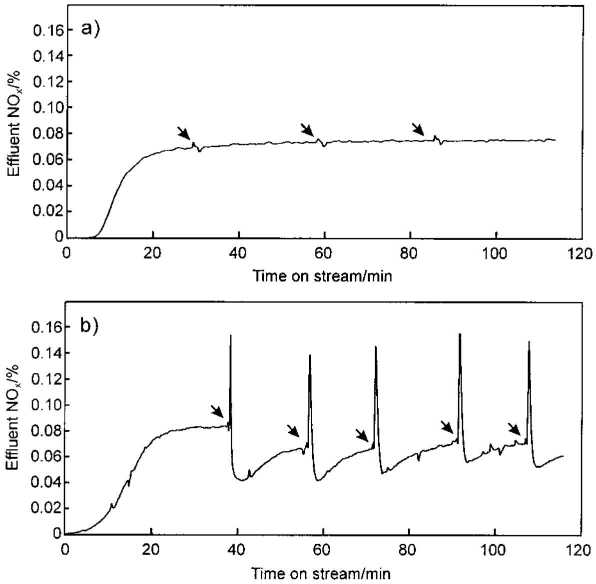

Figure 5. Effect of H_2 pulses on the effluent NO_x from (a) MnO_x−CeO_2 and (b) 1 wt % Pd/A_2O_3 at 150 °C. Each H_2 pulse was 1.0 cm^3. Gas feed: 0.08 vol % NO, 2 vol %O_2, He balance, W/F = 0.24 g·s/cm^3.

Steady-State NO−H_2−O_2 Reactions. The Pd/MnO_x−CeO_2 catalyst was next submitted to the NO−O_2−H_2 reaction in a steady-state flow mode. Figure 6 shows the effect of O_2 concentration on the effluent NO_x from Pd/MnO_x−CeO_2 at 150 °C. Complete removal of NO_x was observed in the absence of O_2. In the presence of O_2, however, effluent NO_x increased slowly from the beginning, the extent depending on the O_2 concentration in the gas feed. The reaction in the presence of 10 vol % O_2 required 14 h to reach a steady-state NO_x concentration (0.052 vol %), where the N_2 evolution corresponds to a selectivity of ~80%. According to the mechanism proposed above, gaseous NO_x is first removed by sorption onto MnO_x−CeO_2, the surface coverage of which increased with reaction time. On the other hand, hydrogen species on impregnated Pd catalysts react mainly with oxygen to produce H_2O, whereas those near the PdO/MnO_x−CeO_2 boundary would be increasingly consumed by the reduction of nitrate adsorbates after the NO_x-sorption is to be saturated. Upon steady

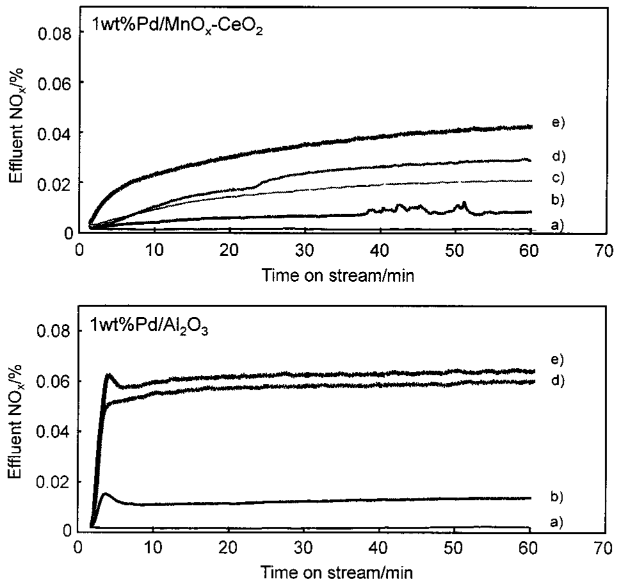

Figure 6. Effluent NO_x from 1 wt % Pd/MnO_x-CeO_2 and 1 wt % $Pd/\gamma-Al_2O_3$ at various O_2 concentrations: (a) 0 vol %; (b) 2 vol %; (c) 4 vol %; (d) 6 vol %; (e) 10 vol %. 0.08 vol % NO, 2 vol % H_2, He balance, W/F = 0.24 g·s/cm^3.

state, therefore, two processes, that is, NO_x-sorption onto MnO_x-CeO_2 and NO_x-H_2 reactions at the boundary, would take place simultaneously, in addition to the H_2 combustion on the Pd catalyst. It is also deduced that the H_2-NO_x reaction requires supplying with each reactant (nitrate and hydrogen) via migration on the solid to the boundary. These complicated and concurrent processes are plausible reasons for the slow derivation of the NO_x concentration in Figure 6.

Figure 6 also shows the comparative results of steady-state $NO-H_2-O_2$ reactions over a $Pd/\gamma-Al_2O_3$ catalyst. Unlike the NO_x breakthrough curve represented in Figure 4b, the effluent NO_x increased immediately after the beginning of the reaction, because the H_2-O_2 reaction took preference of the NO oxidation to NO_2, which is required for sorption onto Al_2O_3. The H_2 combustion became more dominant with an increase of O_2 concentration, resulting in a strong hindrance effect on the $NO-H_2$ reaction. The Pd/MnO_x-CeO_2 catalyst allowed ~65% NO_x-reduction of a stream of 0.08 vol % NO, 2 vol % H_2, and 6 vol % O_2 in He at a low temperature of 150 °C, compared to ~30% for $Pd/\gamma-Al_2O_3$. The different catalyst performances appear to be closely related to the NO_x-sorbability of two support oxides. Due to the lack of NO_x-sorbability on the Al_2O_3 surface, the three reactants (NO_x, H_2, and O_2) must be competitive to adsorb on PdO.

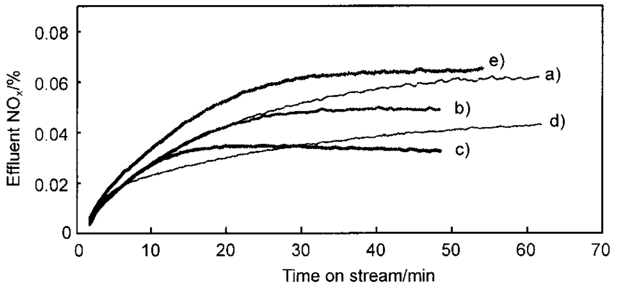

Figure 7. Effluent NO_x from 1 wt % Pd/MnO_x-CeO_2 at various temperatures: (a) 100 °C; (b) 110 °C; (c) 125 °C; (d) 150 °C; (e) 200 °C. 0.08 vol % NO, 2 vol % H_2, 10 vol % O_2, He balance, W/F = 0.24 g·s/cm^3.

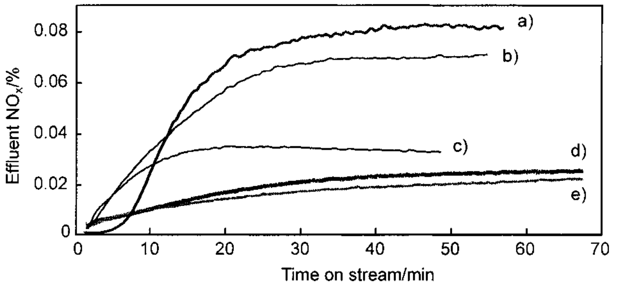

Figure 8. Effluent NO_x from 1 wt % Pd/MnO_x-CeO_2 at various H_2 concentrations: (a) 0 vol %; (b) 1 vol %; (c) 2 vol %; (d) 3 vol %; (e) 4 vol %. 0.08 vol % NO, 10 vol % O_2, He balance, W/F = 0.24 g·s/cm^3.

Table 2. Steady-State $NO-H_2-O_2$ Reaction at 125 °C

catalyst	inlet NO^a/ vol %	NO_x conversion/ %	selectivity/%	
			N_2	N_2O
1 wt % Pd/MnO_x-CeO_2	0.08	62.5	86	14
	0.20	60.4	82	18
0.5 wt %Pd/MnO_x-CeO_2	0.08	9.5	-	-
0.1 wt % Pd/MnO_x-CeO_2	0.08	6.7	-	-
1 wt % Pd/MnO_x	0.08	5.4	-	-
1 wt % Pd/CeO_2	0.08	23.8	54	46

^{a} 2 vol % H_2, 10 vol % O_2, He balance, W/F = 0.24 g·s/cm^3.

The $NO-H_2-O_2$ reaction over 1 wt % Pd/MnO_x-CeO_2 in the presence of 10 vol % O_2 was strongly dependent on temperature, as represented in Figure 7. The high steady-state NO_x conversion of ~60% was attained at 125 °C, but neither an increase nor a decrease of the temperature improved the conversion. This is reasonable when considering the temperature effects on H_2-O_2 and H_2-NO_x reactions and on NO_x-sorption onto MnO_x-CeO_2. As the temperature is raised, the H_2-O_2 reaction should become more dominant, whereas the NO_x-sorption decreases. By contrast, NO_x-sorption increases at lower temperatures, whereas the nitrate thus formed on MnO_x-CeO_2 should become less active toward H_2. The highest NO_x conversion at 125 °C is in good agreement with the N_2 evolution at 120 °C in the TPR study (Figure 2b). Figure 8 exhibits the effect of H_2 concentration on the NO_x removal at 125 °C. The NO_x conversion increased with an increase of the H_2 concentration, but it never exceeded 70%. The reaction continued with no signs of deactivation during 50 h of use. Table 2 summarizes the corresponding product selectivities after 24 h of the reaction. Irrespective of the inlet NO_x concentration, the main product of NO_x reduction was N_2 with >80% selectivity. Nitrous oxide (N_2O) was produced as a byproduct, but no NH_3 was detected. The reaction was also carried out over 1 wt % Pd catalyst impregnated on MnO_x and CeO_2, but the conversions were evidently low in accord with the low NO sorbabilities of these single oxides.

As was pointed out by several researchers,[20-22] Pd is not a selective catalyst for $NO-H_2$ reactions in an oxidizing atmosphere. Nevertheless, the present study

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has demonstrated the selectivity can be much improved by using NO_x-sorbing MnO_x-CeO_2 as a support material. The structure of the active site responsible for selective NO_x-H_2 reactions is not clear at the present stage. However, it was confirmed that combination of NO_x sorbability of MnO_x-CeO_2 and H_2 activation of Pd catalysts produces a synergistic effect to suppress the inhibition from coexisting O_2. According to the previous study,[18] the nitrate adsorbate can occupy almost all the Ce site exposed to the surface. The resulting nitrate-abundant surface near the PdO/MnO_x-CeO_2 boundary, a so-called perimeter site, may be effective in increasing the probability of reactions with hydrogen supplied from Pd catalysts. Provided the H_2-NO_x reaction takes place at the perimeter sites, the activity and selectivity will be affected by the loading of Pd; the higher loading with the same dispersion will produce a large number of the active sites. To verify this hypothesis, the effect of the perimeter sites on the activity was examined by changing the weight of the Pd loading onto MnO_x-CeO_2 (Table 2). Apparently, the activity decreased significantly with decreasing Pd loading ≤ 1 wt %. This is roughly consistent with the selective reduction requiring a large number of the perimeter sites to lie along the PdO/MnO_x-CeO_2 boundary.

Conclusion

The present study has demonstrated an effective use of the NO_x-sorbing MnO_x-CeO_2 to enhance the selectivity of Pd-loaded catalysts toward the NO_x-H_2 reaction in excess O_2. The combination of NO_x sorbability and H_2 activation of each component produces the active sites lying along the PdO/MnO_x-CeO_2 boundary; a high nitrate concentration there would be effective in suppressing the competitive H_2-O_2 reactions. Our concept on NO_x-sorptive catalysts achieved in the present study may be broadly applied to the development of various catalyst/NO_x-sorbent combinations for low-temperature NO_x reduction in a strongly oxidizing atmosphere.

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