

Reversible Sorption of Nitrogen Oxides in Mn–Zr Oxide

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Removal of NO (900 ppm) was investigated using several mixed metal oxide systems in the presence and absence of gaseous O₂. At 200–300°C Mn–Zr oxide exhibited the highest NO removal among the oxides investigated and it was facilitated in the presence of O₂. The removal was accompanied by the sorption of oxidized NO species on or in the solid and stored via formation of nitrate. Since the sorption and desorption was reversible, the oxide sorbent was regenerated on heating the sample at 400°C after NO uptake. The stored NO_x species were also eliminated from the solid by reduction with C₃H₈ or C₂H₅OH at 300°C. The amorphous phase of the Mn–Zr oxide which is formed after heating this oxide at 450°C was extremely effective for NO removal due to good mixing between Mn and Zr oxides. The surface area of the oxide was a maximum and the amorphous phase was dominant for the oxide with Mn/Zr = 1. The removal of NO was not influenced by coexisting CO₂ and was promoted by the presence of H₂O. © 1996 Academic Press, Inc.

INTRODUCTION

Removal of NO_x from exhaust gases is a crucial problem for solving acid rain and other air pollution problems in the atmosphere. For large power stations, selective catalytic reduction (SCR) of NO_x with ammonia is now well-established technology (1). However, for relatively small scale combustors for cogeneration systems or on-site generators, the high capital cost for the SCR with ammonia and the possibility of a slip of ammonia become problems. Three-way catalysts have been widely used for cleaning automotive exhaust when gasoline engines are operated near the stoichiometric air/fuel ratio (2). However, a new and innovative process has been requested for cleaning exhaust gases from diesel-powered vehicles and those with lean fuel engines. These applications require a catalyst to be operated under oxidative conditions. Selective reduction of NO_x with hydrocarbons has been actively investigated recently by many researchers (3, 4). Cu-exchanged ZSM-5 (5, 6), metallosilicates (7), alumina (8), and metal-exchanged zeolites (9–11) have been reported to be active for this reaction. However, SCR with hydrocarbons has

not been commercialized up to now due to problems of catalyst deactivation by the coexisting gases, such as H₂O and SO₂ (12, 13). This difficulty is to some extent related to the very dilute concentration of NO_x in exhaust gases. One possible answer to overcome this difficulty by a dry process would be to decouple the separation of NO_x from the flue gas with catalytic NO_x conversion. In the initial step, nitrogen oxides are removed from the gas phase and stored in a solid. Then the catalytic converter, e.g., the selective reduction of NO_x by a 3-way catalyst and decomposition of NO (14), is operated when NO is released from the solid in the second step, without being affected by the coexisting large amounts of oxygen or water. A similar concept has been commercialized in the NO_x-storage reduction catalyst proposed by the research group of Toyota Motors (15). The 3-way catalyst was combined with a NO_x storage material such as Ba-oxide in their catalyst. Nitrogen oxides are first stored in the solid in the oxidized form during the cruising of an automobile in lean-burn condition. Then, the stored NO_x is released and reduced by the 3-way catalyst when the atmosphere is changed intermittently to the stoichiometric air/fuel ratio. This application suggests the importance of investigating a reversible NO absorbent or adsorbent in the catalytic conversion of NO_x. Another possibility is to treat the concentrated NO_x by a wet process. The present investigation aims at removal of NO_x from dilute gaseous mixture to form concentrated nitrogen oxides by sorption–desorption cycles of a solid oxide. Nitrogen oxides are stored in the solid until the metal oxide is converted into the corresponding nitrate salt, whereupon stored NO_x is again released into the gas phase in a concentrated form on heating the solid. A related phenomenon has already been reported for Y–Ba–Cu–O (16), Ba–Cu–O (17), and Y–Sr–Co–O (18) systems. These oxides have been reported to be active for removal of a large amount of NO_x by absorption, but deactivation of the absorbents is expected because of the formation of surface carbonate in the presence of CO₂. The rare earth and alkaline earth metal cations in these oxide systems serve as strong absorption sites for CO₂ due to their strong basicity. We have tried to develop materials

for NO_x absorption which do not contain rare earth and alkaline earth components. In this paper, novel sorption–desorption properties of Mn–Zr oxides are reported for application to NO_x removal.

EXPERIMENTAL

Mixed oxide samples were prepared by coprecipitation from a solution of the corresponding nitrate mixtures. Various mixed oxide samples were calcined at 450°C prior to the NO removal experiments. For the preparation of Mn–Zr oxides, the calculated amounts of Mn(NO₃)₃ and ZrO(NO₃)₂ (Kishida Chemical, Guaranteed reagent grade) were dissolved in water. After adding aqueous ammonia to the nitrate solution, the solution with the precipitate was evaporated to dryness and then heated at 450°C for 6 h. The powder thus obtained was sieved to 10–20 mesh.

Sorption and desorption experiments of NO were carried out in a flow system. Nitrogen monoxide was diluted in He and sometimes mixed with O₂ before admission to a quartz tube reactor. The uptake and desorption characteristics of NO_x were tested in the temperature range from 200 to 400°C at a contact time of 0.6–1.0 g s cm⁻³ using 1 g of the mixed oxide sample. When required, CO₂, H₂O, and/or C₃H₈ was added to the gaseous mixture. The concentration of NO_x was analyzed with a chemical luminescence type NO_x meter (Shimadzu, NOA305). The effluent gas was generally passed through a carbon reactor to reduce NO₂ for analysis of the sum of NO and NO₂ concentrations before it was supplied to the NO_x meter. The gaseous composition of the inlet and outlet mixture was also analyzed by gas chromatography. The phase in the sample was identified with an X-ray diffractometer (Rigaku, RINT-1400).

RESULTS AND DISCUSSION

Removal of NO by Mixed Metal Oxides

Removal of NO was investigated both in the presence and in the absence of O₂ at 200°C in NO (900 ppm) for several oxide materials containing Mn and/or Zr as listed in Table 1. Only the oxides which exhibited a higher removal of NO in the presence of O₂ than in the absence of O₂ after 30 min from the start of the reaction are listed in the table since the present investigation aims at NO removal in air. The mechanism of NO removal was not taken into account at this stage; some oxides are active for decomposition of NO and some are effective in absorption or adsorption. In the series of oxides studied, the Mn–Fe, Mn–Cr, Mn–Zr, and Mn–Cu systems exhibited a relatively high removal of NO. The Mn–Zr oxide exhibited the highest removal of NO both with and without O₂. Nitrogen monoxide was scarcely detected in the outlet gas after

TABLE 1

NO Removal by Mixed Oxides Containing Mn and/or Zr

Oxide	NO removal ^a (%)	
	0% O ₂	10% O ₂
MnOx · Al ₂ O ₃	9.9	14.8
MnOx · Cr ₂ O ₃	0	2.2
MnOx · CuO	0	10.2
MnOx · Fe ₂ O ₃	11.9	37.4
MnOx · MoO ₃	5.9	15.2
MnOx · TiO ₂	0	25.0
MnOx · ZrO ₂	100.0	100.0
ZrO ₂ · Al ₂ O ₃	0	8.7
ZrO ₂ · Cr ₂ O ₃	0	14.3
ZrO ₂ · CuO	2.7	27.0
ZrO ₂ · Fe ₂ O ₃	0.4	8.7
ZrO ₂ · MoO ₃	0.3	2.4
ZrO ₂ · TiO ₂	7.6	17.4

Note. Calcination temperature 450°C. 0.1 vol.% NO, 0 or 10% O₂, He balance. Reaction temperature 200°C, W/F = 1 g s cm⁻³.

^a NO removal after 30 min of use.

passing through this oxide during the initial 30 min. Detailed NO removal characteristics and mechanisms were accordingly investigated for the Mn–Zr system.

NO-Sorptive Properties for Mn–Zr Oxide

The time course of the NO removal for the Mn–Zr oxide is shown in Fig. 1. Nitrogen monoxide (900 ppm) and oxygen (10%) was supplied to the Mn–Zr oxide (Mn/Zr = 1) at 200°C. Most of the NO was removed during the initial 60 min, then the concentration of NO at the outlet gradually increased with an elapse of time. The sample no longer showed a removal property after 6 h

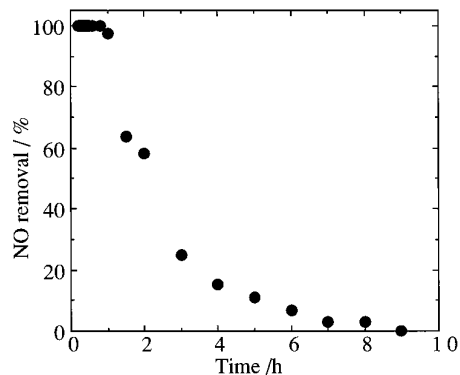


FIG. 1. Time course of NO removal by Mn–Zr oxide (Mn/Zr = 1). 900 ppm NO, 10% O₂, He balance. Reaction temperature 200°C. W/F = 1 g s cm⁻³.

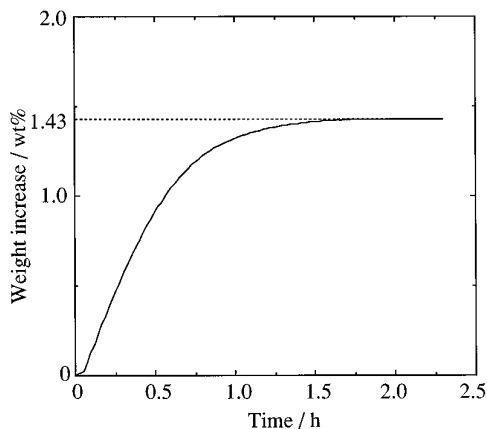


FIG. 2. Weight change of Mn-Zr oxide (Mn/Zr = 1) during NO removal. 850 ppm NO, 10% O₂, He balance. Reaction temperature 200°C.

from the start of the experiment. The total amount of NO removed in 6 h of operation was 14.7 cm³ (STP)/g which corresponds to 0.133 mol-NO/mol-Zr.

In comparison with the removal capacity measured from the gas-phase NO concentration, a gravimetric analysis was carried out during the NO removal as shown in Fig. 2. Nitrogen monoxide (850 ppm) was supplied to the Mn-Zr oxide (Mn/Zr = 1) in the presence of O₂ (10%) at 200°C. The weight of the Mn-Zr oxide increased with time during the uptake of NO from the gas phase. Thus, the NO removal is assumed to proceed by sorption of NO_x species in the Mn-Zr oxide solid. The weight increase became gradual with time approaching a constant value. The amount of sorption after saturation was 1.43 wt.% of the original oxide which corresponded to 0.047 mol-NO₃/mol-Zr. The amount of sorption was assumed to be due to the formation of oxidized NO species as discussed later. The NO uptake measured by the gravimetric analysis was somewhat smaller than that from the tubular reactor by gas-phase analysis. The difference in storage capacity for the two measurements is probably due to gas supply in the macropores. The NO-containing gas was forced to pass through a solid bed for the tubular reactor, whereas the gas diffused in a powder agglomerate in the case of the gravimetric analysis. As we have reported previously, absorption of NO in Ba-Cu oxide or Ba-Cu-Mn oxide proceeds via oxidation of NO and the formation of nitrate in the solid bulk (17). The present NO uptake for Mn-Zr oxide resembles the previous system and is expected to proceed also by the formation of nitrate, as explained later.

The sorptive properties of the Mn-Zr oxides for NO were investigated using samples with different Mn/Zr ratios (Table 2). The removal curves were basically similar to that shown in Fig. 1. The NO removal was 100% for every Mn-Zr oxide at the start of the NO supply and then gradually decreased after 10 to 60 min of operation. The

start of the decrease and therefore the sorption capacity was quite dependent on the Mn/Zr ratio of the oxide. The amount of stored NO was largest for the sample with Mn/Zr = 1 but decreased on either decreasing or increasing the Mn/Zr ratio. The addition of noble metals was not effective in promoting the absorption capacity and absorption rate, as can be seen in Table 2.

The X-ray diffraction patterns of Mn-Zr oxides with different Mn/Zr ratios after calcination at 450°C are shown in Fig. 3. At the Mn-rich compositions, very weak diffraction lines of MnO₂ were detected in the pattern. Diffraction lines from ZrO₂ or reaction products was not observed at Mn/Zr > 1/5. The sample at Mn/Zr = 5 consisted of Mn₂O₃ and Mn₅O₇ phases. Only a weak diffraction line of Mn₂O₃ was observed for the sample with Mn/Zr = 1 in addition to a broad halo from an amorphous phase. For the sample with Mn/Zr = 1/5, diffraction lines from the ZrO₂ phase appeared and these were intensified at the ZrO₂ rich composition. In every sample except the Zr-rich sample (Mn/Zr = 1/9), the diffraction lines are very broad and weak, indicating poor crystallinity due to the low calcination temperature. It is noted that the halo from the amorphous phase was evident for the samples at or near Mn/Zr = 1.

The surface areas of the Mn-Zr oxide are also listed in Fig. 3. The surface area was high and at maximum at Mn/Zr = 1. The formation of the amorphous phase is expected to be related to the large surface area. The X-ray diffraction pattern and NO removal measurement imply that the amorphous phase which is dominant at Mn/Zr = 1 is especially active for removal of NO, since the amount of NO uptake was maximum at the composition with strong appearance of the halo. The large surface area is also effective in accelerating the removal of NO.

Sorption-Desorption Behavior of Mn-Zr Oxide

The NO removal characteristics were investigated during programmed heating of the Mn-Zr oxide with a con-

TABLE 2
Capacity of Mn-Zr Oxides for NO Removal

Sample	Capacity for NO removal mol/mol-Zr
Mn-Zr oxide (Mn/Zr = 5)	0.105
Mn-Zr oxide (Mn/Zr = 1)	0.133
Mn-Zr oxide (Mn/Zr = 1/5)	0.034
Mn-Zr oxide (Mn/Zr = 1/9)	0.029
1 wt% Pt/Mn-Zr oxide (Mn/Zr = 1)	0.058
1 wt% Rh/Mn-Zr oxide (Mn/Zr = 1)	0.035
1 wt% Ru/Mn-Zr oxide (Mn/Zr = 1)	0.042
1 wt% Pd/Mn-Zr oxide (Mn/Zr = 1)	0.073

Note. Calcination temperature 450°C. 900 ppm NO, 10% O₂, He balance. Reaction temperature 200°C, W/F = 1 g s cm⁻³.

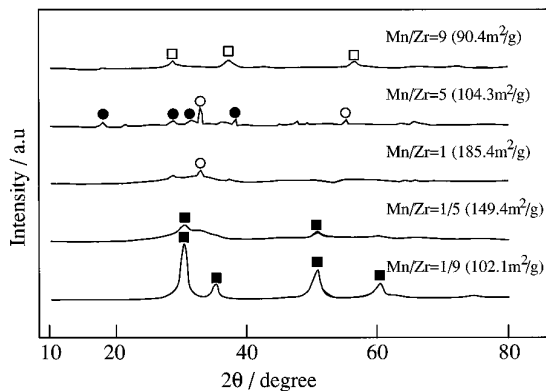


FIG. 3. XRD pattern of Mn/Zr oxides with different Mn/Zr ratios after heating at 450°C. Values in parentheses are surface areas. (○) Mn_2O_3 , (□) MnO_2 , (●) Mn_3O_4 , (■) ZrO_2 .

stant rate (Fig. 4). The Mn-Zr oxide sample was heated at 100°C and exposed to the atmosphere of flowing NO (900 ppm) with O_2 (10%) and then heated at the constant rate of 10°C/min. The removal of NO proceeded below 300°C. The outlet concentration of NO was almost zero as shown in the figure. The concentration of NO in the gas-phase sharply increased from 320°C, then exceeded the value of the feed gas. This behavior confirms that the removal of NO for this system proceeds by sorption of NO or oxidized NO_x species in the solid and the desorption occurs at elevated temperatures. The outlet concentration of NO sharply decreased after passing through a maximum at 400°C and reached again to the initial concentration level from 500°C. Neither desorption nor sorption proceeded above 500°C. The sorption-desorption therefore appears reversible in this experiment.

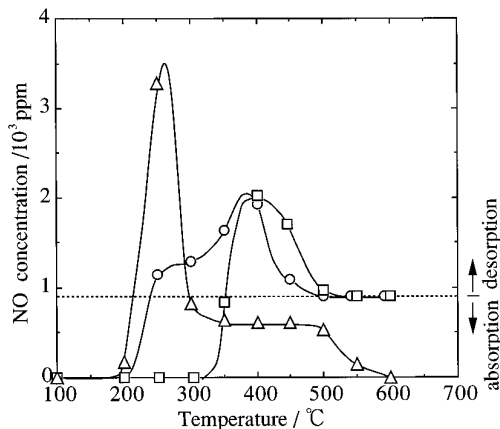


FIG. 4. Sorption-desorption curve of NO for Mn-Zr oxide (Mn/Zr = 1) during programmed heating in different atmospheres after sample was heated at 450°C for 6 h. (○) 900 ppm NO, (□) 900 ppm NO + 10% O_2 , (Δ) 900 ppm NO + 1500 ppm C_3H_8 , He balance. W/F = 1 g s cm^{-3} . (---) initial concentration of NO.

The temperature-programmed sorption-desorption curves in other atmospheres in which the sample was heated in NO (900 ppm) + He and in NO (900 ppm) + C_3H_8 (1500 ppm) + He are also shown in Fig. 4. In every case, the removal of NO proceeded at low temperatures; thus the NO concentration in the outlet gas was almost zero. With increasing temperature, the NO concentration rose abruptly, indicating desorption of NO. The temperature of the transition from uptake to desorption was quite sensitive to the atmosphere. The desorption started from the lowest temperature in the reducing atmosphere with C_3H_8 , whereas the desorption started from the highest temperature in the O_2 -containing atmosphere. It is obvious that the start of the desorption began at lower temperatures as the experiment was operated in more reducing atmosphere. In other words, the oxidizing atmosphere stabilizes the sorbed species. It is expected that the uptake of NO proceeds via oxidation of NO and the formation of nitrate, as was previously proposed for the Ba-Cu oxide system (17). The final concentration at high temperatures agreed with the initial concentration of NO in the case of NO + O_2 + He and NO + He, since neither sorption nor desorption occurs in the high temperature region. Only in the case of NO + C_3H_8 + He was the concentration of NO lower than the inlet value in the temperature range from 300 to 600°C. The concentration of NO at 600°C reached zero again. In this region, gas chromatographic analysis indicated that desorbed nitrogen oxide was reduced to N_2 with C_3H_8 . It is well known that NO can be easily reduced to N_2 by the catalytic process in the stoichiometric air/fuel mixture and in more reducing atmospheres.

The reversibility of the absorption and desorption was tested at a fixed temperature by supplying a gaseous mixture of NO (900 ppm) and O_2 (10%) to the Mn-Zr oxide (Mn/Zr = 1) at 200°C (Fig. 5). Nitrogen monoxide was completely removed from the gas phase for the initial 60 min. Then, the sample was exposed to He and heated within 30 min to 400°C. The sample was kept at 400°C in He until the stored NO_x was completely eliminated. The amount of NO uptake (0.047 mol/mol-Zr) almost agreed with that of desorption (0.044 mol/mol-Zr), indicating that the sorption and desorption is almost reversible.

The gas-phase analysis indicated that only nitrogen monoxide was released in the desorption step in most cases. There may be several possible desorption species, but nitrous oxide (N_2O) was scarcely observed by gas chromatography during the desorption experiment. Of two other desorption species, i.e., NO and NO_2 , only nitrogen monoxide is generally released due to its stability in the desorption condition of high temperature or reducing atmosphere. The desorption species appear to be determined by the thermodynamic stability of NO and NO_2 since Mn readily equilibrates gas-phase nitrogen oxide species.

The temperature-programmed sorption-desorption ex-

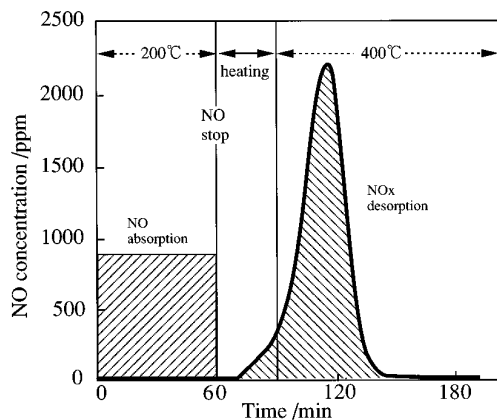


FIG. 5. Amounts of NO sorbed in Mn-Zr oxide ($Mn/Zr = 1$) at 200°C and desorbed at 400°C. Hatched areas indicate amounts of NO sorbed and desorbed. Sorption condition: 900 ppm NO, 10% O_2 , He balance. $T = 200^\circ C$ (60 min), $W/F = 0.6 \text{ g s cm}^{-3}$. Desorption condition: 200°C \rightarrow 400°C and at 400°C in He.

periments in different atmospheres suggest that the reduction of stored species facilitates the desorption of NO_x . In addition to the thermal desorption, the reduction treatment is considered as an alternative method to recover the oxide solid after the NO uptake. The NO sorption was carried out in NO (900 ppm) for 10 min at 300°C in the presence of O_2 (10%), then the atmosphere was switched to the reducing atmosphere of C_3H_8 or C_2H_5OH at the same temperature, as shown in Fig. 6. The removal of NO was 100% for 10 min. The desorption peak which appeared after switching the atmosphere was more sharp in the C_3H_8 atmosphere than in C_2H_5OH . The amount of removed NO was $8.1 \times 10^{-3} \text{ mol/mol-Zr}$, whereas the desorption

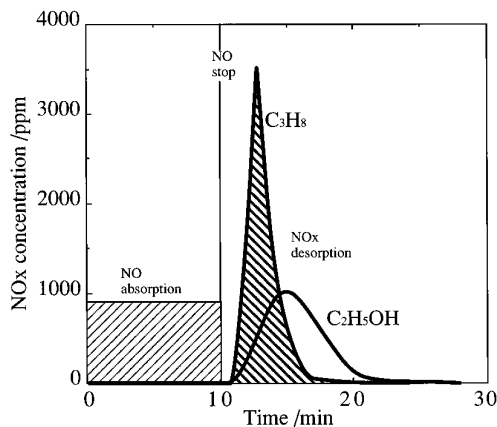


FIG. 6. Amounts of NO sorbed in Mn-Zr oxide and desorbed in reducing atmospheres. Sorption condition: 900 ppm NO, 10% O_2 , He balance. $T = 300^\circ C$ (10 min). $W/F = 0.6 \text{ g s cm}^{-3}$. Desorption condition: 1500 ppm C_3H_8 or 1500 ppm C_2H_5OH , He balance, $T = 300^\circ C$ and $W/F = 0.6 \text{ g s cm}^{-3}$.

amounted to $7.0 \times 10^{-3} \text{ mol-NO/mol-Zr}$ for C_3H_8 and $4.4 \times 10^{-3} \text{ mol-NO/mol-Zr}$ for C_2H_5OH , namely only 86 and 55% of NO was reversibly desorbed, respectively. The remaining parts were reduced with C_3H_8 or C_2H_5OH and therefore the formation of N_2 was detected in the outlet gas by gas chromatography. It is noted from the comparison of Figs. 5 and 6 that the desorption proceeds more rapidly in the reducing atmosphere than in the case of He. The desorption was completed within 25 min at 300°C by using C_3H_8 or C_2H_5OH , even though the temperature was low. For the recovery of the oxide, the treatment in the controlled reducing atmosphere is more effective and easier than the treatment of the sample at high temperatures. If the desorption atmosphere is set within the operation window of the 3-way catalyst or at the NO reduction condition, the desorbed gas can be directly introduced to the catalytic converter.

Mechanism of NO Uptake

The removal of NO obviously proceeded by the formation of nitrate-like species on or in the solid. It is not conclusive from the present study whether the NO uptake is a surface or a bulk reaction. The overall amount of removed NO attained for the oxide with $Mn/Zr = 1$ ($0.133 \text{ mol-NO/mol-Zr}$) is too large to be explained by a surface monolayer reaction. However, the extraordinary large surface area and the amorphous formation at this composition still suggest the possibility of surface adsorption with surface reaction. The X-ray diffraction pattern after sorption remained amorphous; therefore bulk nitrate formation could not be judged by this method. An infrared spectrum after absorption of NO exhibited a sharp absorption band at 1380 cm^{-1} which is attributed to the NO_3^- species on or in the solid (19). The behavior of NO removal resembles that observed in the alkaline earth or rare earth oxide containing systems in which bulk reaction is reported to be operative (17, 18).

The NO uptake for the Mn-Zr oxide is expected to be initiated by the catalytic oxidation of NO to NO_2 . The oxidation activity for NO to NO_2 and NO_3^- is therefore important for this type of NO removal system. The oxidation of NO to NO_3^- ion appears to proceed via the formation of NO_2 on the solid surface. The catalytic oxidation of NO was tested in the flow system using pure Mn oxide. The temperature dependence of the oxidation activity is shown in Fig. 7. The equilibrium conversion of the reaction $NO + 1/2 O_2 \rightleftharpoons NO_2$ in 10% O_2 is shown by the solid line in the figure. The conversion of NO increased initially as the catalyst became reactive and reached equilibrium level at or above 200°C within the experimental error, indicating the high activity of Mn oxide for NO oxidation to NO_2 . Thus, the Mn species in Mn-Zr oxide serves as an oxidation catalyst in the presence of oxygen. The NO absorption

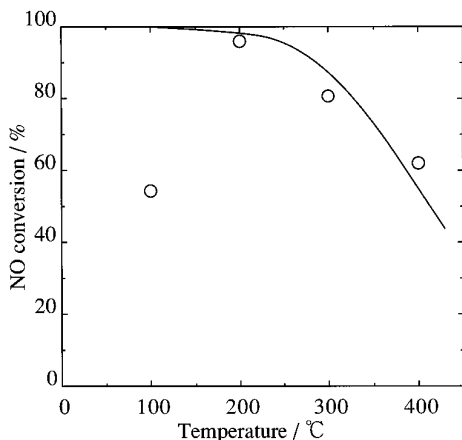


FIG. 7. Activity of Mn oxide catalyst for oxidation of NO to NO₂. 900 ppm NO, 10% O₂, He balance. W/F = 1 g s cm⁻³. (—) equilibrium conversion.

also proceeded in the absence of gaseous O₂, as can be seen in the low temperature region of Fig. 4. The valence of Mn oxide is known to be very sensitive to the change in atmosphere and temperature in the present reaction conditions. Therefore, oxygen species present in the Mn oxide lattice before the NO uptake is used for oxidation of NO and subsequent sorption. Thus the sorption is continued until the available lattice oxygen is consumed.

Effect of Coexisting Gases on Removal of NO

The effect of coexisting gas is especially important because NO absorption is desired to be applied for cleaning exhaust gases from combustors. The removal of NO₂ was first investigated because the exhaust gas generally contains a nonequilibrated mixture of NO and NO₂. In the present system, the removal of NO is suggested to be initiated by the oxidation of NO to NO₂ on the surface. Therefore, the removal of NO₂ is expected to proceed easily on the Mn-Zr oxide, which is confirmed from the comparison of curves for NO and NO₂ removal in Fig. 8. The curve for NO₂ removal was almost similar to the case of NO removal. The overall amount of NO₂ uptake (0.107 mol/mol-Zr) was slightly larger than that of NO (0.082 mol/mol-Zr).

The behavior of NO removal was also tested in the presence of CO₂ and H₂O, since these gases are always present in exhaust gas (Fig. 9). Many solid oxide absorbents which operate at high temperatures deteriorate in the presence of these gases. Our previous study on Cu-Ba or Cu-Mn systems showed no obvious deterioration with CO₂ within a few days, but long operation in CO₂ atmosphere gradually deactivated the absorption capacity due to strong bonding between CO₂ and alkaline earth or rare earth cations (17). However, in the present Mn-Zr system, the

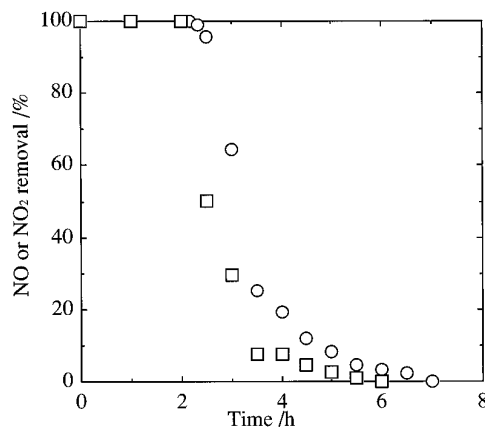


FIG. 8. NO and NO₂ removal curves for Mn-Zr oxide (Mn/Zr = 1). 10% O₂, He balance. $T = 200^{\circ}\text{C}$, W/F = 1 g s cm⁻³. (○) NO and (□) NO₂ removal.

sorption curve and total amount of uptake was hardly affected in the presence of CO₂ (10%) as shown in Fig. 9. This NO storage system contains neither alkaline earth nor rare earth ions, so the deterioration by CO₂ was negligibly small.

The behavior in the presence of H₂O is also shown in Fig. 9. The NO removal in the first 130 min was scarcely affected by the presence of H₂O in the atmosphere, and the removal rate remained high even after 3 h from the start of the reaction. The overall amount of uptake was obviously enhanced with H₂O. It is important that the sorption is promoted in the presence of H₂O because combustion exhaust always contains moisture. The adsorbed or absorbed water molecules appear to stabilize sorbed nitrate ions through hydration and to facilitate gas-solid reaction by promotion of diffusion. However, a detailed

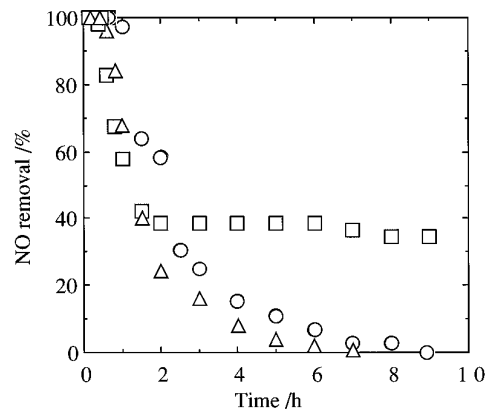


FIG. 9. Time course of NO removal with or without CO₂ or steam for Mn-Zr oxide (Mn/Zr = 1). (○) 900 ppm NO, 10% O₂; (□) 900 ppm NO, 10% O₂, 10% CO₂; (△) 900 ppm NO, 10% O₂, 10% H₂O; He balance. $T = 200^{\circ}\text{C}$, W/F = 1 g s cm⁻³.

investigation is necessary for the exact understanding of the promotion effect of H₂O.

CONCLUSION

The present investigation has indicated the possibility of Mn–Zr oxide as a new material for sorption of NO_x. The sorption–desorption behavior of solids has not been investigated satisfactorily so far because research on NO_x removal has been mainly focused on the development of the catalytic process. The present system proposed a possibility of the combination of a catalytic process with the separation process which is based on the sorption–desorption cycle. The catalytic conversion of concentrated NO eliminates most of the difficulty encountered for the selective catalytic reduction of NO by hydrocarbons and catalytic NO decomposition. The most attractive characteristics of the present NO storage system are the tolerance to CO₂ and the promotion of NO removal with O₂ and H₂O, since these gases are always existing in the exhaust gases. The sorption in the present system is basically a gas–solid reaction; therefore the removal capacity is large. However, the rate of removal is affected by the extent of mixing between Mn- and Zr-oxides and the surface area of the mixed oxide. In this respect, the sorption material should be designed both with control of microstructure and selection of its components. The development of reactor design is also necessary to apply this reversible sorption–desorption cycle as the preceding separation step to the catalytic conversion process.

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