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Catalysis Today 84 (2003) 201–207

CATALYSIS TODAY

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NO_x storage and reduction characteristics of Pd/MnO_x–CeO_2 at low temperature

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Abstract

The reaction between hydrogen and NO was studied over 1 wt.% Pd supported on NO_x-sorbing material, MnO_x–CeO_2, at low temperatures. The result of pulse mode reactions suggest that NO_x adsorbed as nitrate and/or nitrite on MnO_x–CeO_2 was reduced by hydrogen, which was spilt-over from Pd catalyst. The NO_x storage and reduction (NSR) cycles were carried out over Pd/MnO_x–CeO_2 in a conventional flow reactor at 150 °C. In a storage step, NO was removed by the oxidative adsorption from a stream of 0.04–0.08% NO, 5–10% O_2, and He balance. This was followed by a reducing step, where a stream of 1% H_2/He was supplied to ensure the conversion of nitrate/nitrite to N_2 and thus restore the adsorbability. It was revealed that the NSR cycle is much more suitable for the H_2–deNO_x process in excess O_2, compared to a conventional steady state reaction mode.

Keywords: NO_x storage and reduction; H_2–NO reaction; NO_x-sorbing material

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1. Introduction

Interest in the application of NO_x-sorbing materials for emission control has increased markedly in the past decade [1,2]. A successful example taking advantage of the NO_x-sorbing process can be seen in the so-called "NO_x storage and reduction (NSR) catalysts", which have been developed by Toyota researchers for automotive deNO_x in excess O_2 [3]. In the catalyst system under oxidizing atmosphere (lean conditions), NO is absorbed by an alkali component (Ba) dispersed on the catalyst surface.

$$NO + O_2 + Ba\text{–}O \xrightarrow{Pt} Ba\text{–}NO_x$$

This is followed by a short period of rich condition supplying reducing exhaust, during which thermal desorption of NO_x and subsequent reduction to N_2 take place on Pt catalysts.

$$Ba\text{–}NO_x + HC \xrightarrow{Pt} Ba\text{–}O + N_2 + H_2O + CO_2$$

The sorption–reduction cycle is repeated periodically by controlling the air:fuel ratio to lean or rich conditions. The NSR catalyst system has been turned out to be most successful for gasoline engines operated at lean-burn conditions. This example suggests that NO_x-sorbing catalysts having integrated structures of NO adsorption sites and catalytically active sites would be possible. Inspired by this work, several combinations of NO_x-sorbing materials and reducing catalysts have been studied by other research groups [4–7]. Unfortunately, however, none of such catalyst systems reported so far can be used at low temperatures below 150 °C.

In our previous work, we studied the sorption/desorption properties of NO over MnO_x–CeO_2 solid solutions with the fluorite-type structure. The oxides

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doi:10.1016/S0920-5861(03)00275-X

are useful as not only a NO_x-adsorbing material, but also a support material that allows Pd to catalyze $NO–H_2$ reactions in the presence of excess O_2. 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% NO, 2% H_2, and 6% O_2 in He at a low temperature of 150 °C, compared to ca. 30% for Pd/γ–Al_2O_3, the reaction on which was more suppressed by competitive $H_2–O_2$ reaction. These bifunctional surface structures produced by the combination of NO_x sorbability of $MnO_x–CeO_2$ and H_2 activation of Pd catalysts are expected to give rise to a synergistic effect in selective deNO_x processes. The focus of the present study is to apply the Pd/$MnO_x–CeO_2$ catalyst to the NSR cycles at 125 °C. The catalytic performance was compared to that obtained for conventional steady state $NO–H_2–O_2$ reactions.

2. Experimental

The equimolar binary oxide, $MnO_x–CeO_2$, was prepared by coprecipitation from aqueous solutions of nitrates [8–11]. Calculated amounts of $Mn(NO_3)_2\cdot 6H_2O$ and $Ce(NO_3)_3\cdot 6H_2O$ (Wako Chemicals, Guaranteed reagent grade) were dissolved in distilled water. Addition of 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 (1 wt.% loading as Pd metal). As prepared catalyst powders were shaped into 20 mesh granules and heated at 400 °C in flowing 10% O_2/He or 5% H_2/He for 1 h before use.

The NO adsorbability and the reactivity of adsorbed NO_x to H_2 were evaluated in pulse mode reactions in a flow reactor. The Pd-loaded or unloaded sample (0.2 g) was placed in a stream of 0.08% NO 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. The NSR cycle was carried out by alternating two different gas feeds to the catalyst bed. First, gas mixtures of NO (0.04 or 0.08%), O_2 (5 or 10%), and He balance were supplied at $W/F = 0.24\,s\,g\,cm^{-3}$ during a storage step (9 or 10 min). This was followed by a reduction step (3 or 2 min), in which the gas feed was changed to 1% H_2/He at $W/F = 0.24\,s\,g\,cm^{-3}$. The reactor effluent was analyzed continuously by a chemiluminescence NO_x analyzer. The resultant profiles for effluent NO_x concentration were compared with those for steady state NO (0.08%)–H_2 (0.24–2%)–O_2 (5–10%) reactions, which were also carried out in the flow system. NO_x (NO/NO_2) and other gas species were analyzed by using a chemiluminescence NO_x analyzer, a gas chromatograph (TCD, Molecular Sieves-5A and Porapak-Q columns), and a mass spectrometer.

3. Results and discussion

3.1. $NO–H_2$ reaction over Pd/$MnO_x–CeO_2$

The Pd-loaded $MnO_x–CeO_2$ has been shown to be an effective NO storage–reduction bifunctional catalyst, which can be applied to low temperature deNO_x processes [8,9,12]. Fig. 1 shows the typical examples of NSR by H_2, which were measured by pulse mode reactions. In this measurement, 1 wt.% Pd/$MnO_x–CeO_2$, which was treated in a stream of 5% H_2/He or 10% O_2/He at 400 °C, was placed in a flowing gas mixture of 0.08% NO/He at 150 °C with monitoring NO_x concentration in the reactor effluent. The NO_x concentration increased gradually at the beginning to give a breakthrough curve of NO uptake. The catalyst after saturated by adsorptive NO uptake was submitted to the micropulse injection of H_2 ($1\,cm^3$) as indicated by arrows in Fig. 1. The injection of H_2 pulses immediately led to a drop of the NO_x concentration, which was then increased slowly as was observed before the H_2 pulse to give rise to a large negative peak. The area of this negative peak corresponds to the maximal amount of NO adsorbed by $MnO_x–CeO_2$ (ca. $0.1\,mmol\,g^{-1}$). This peak was accompanied by the evolution of corresponding amount of N_2, suggesting the conversion of NO_x adsorbates on $MnO_x–CeO_2$ to N_2.

Fig. 2 illustrates the model to explain the results of the pulse reactions over Pd/$MnO_x–CeO_2$ catalyst [13]. First, the surface of $MnO_x–CeO_2$ is covered predominantly with nitrite (NO_2) and/or nitrate (NO_3) as a result of oxidative adsorption of NO; NO rapidly occupies ca. 30% of Ce site exposed on the surface.

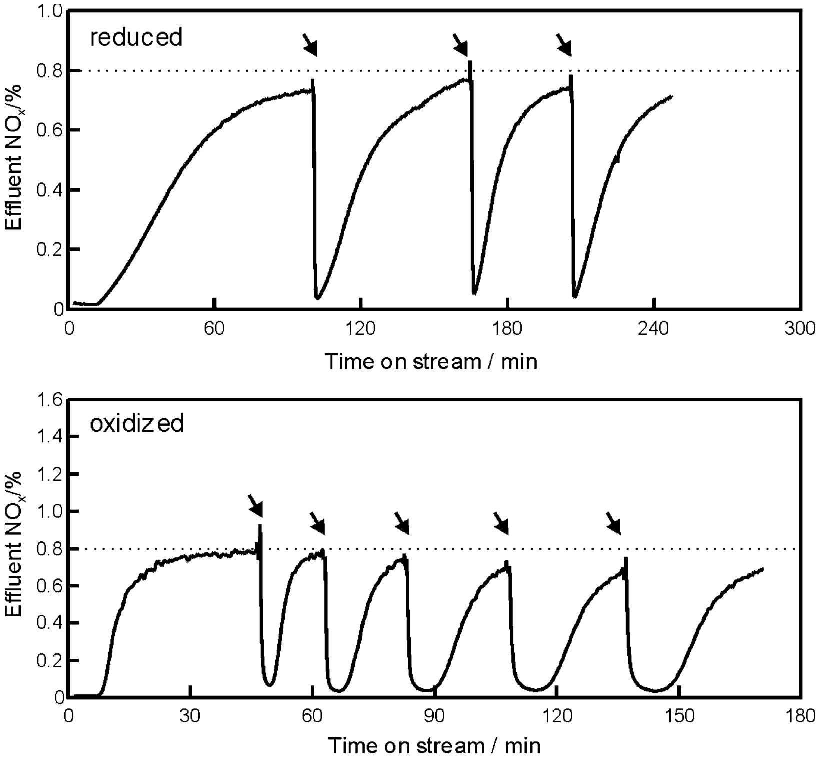

Fig. 1. Effect of H_2 pulses on effluent NO_x from 1 wt.% Pd/MnO_x–CeO_2 at 150 °C. Each H_2 pulse was $1.0\,cm^3$; Gas feed: 0.08% NO, 2% O_2, He balance, $W/F = 0.24\,s\,g\,cm^{-3}$. The sample was treated at 400 °C in a flowing 10% O_2/He (oxidized) or 5% H_2/He (reduced) before use.

Soon after this, the nitrite/nitrate species thus formed can be reduced by H_2, which is dissociatively adsorbed onto Pd and subsequently spills over onto MnO_2–CeO_2. At 150 °C, the amount of hydrogen spilt-over exceeds 300 times larger than the number of Pd atoms exposed on the surface [12,13]. Finally, the spilt-over hydrogen brings about the reduction of the NO_x adsorbing thereon to N_2. This is the reason why the injection of H_2 pulses caused the large negative peaks as shown in Fig. 1. It should be noted that the area of negative peaks is sensitive to the catalyst pretreatment; i.e. the reduced catalyst constantly yielded very large negative peaks, whereas, for oxidized catalyst, the peak was initially small and became larger with the number of pulsing. This means that the part of H_2 injected is initially consumed to reduce PdO as well as MnO_x–CeO_2. After the third injection, the area of each peak became almost constant and comparable to the reduced catalyst case.

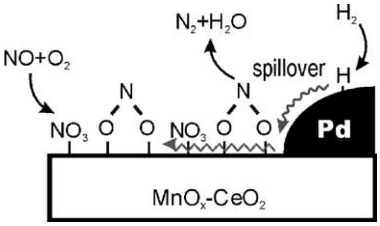

Fig. 2. A possible model for reaction between H_2 and adsorbed NO_x over Pd/MnO_x–CeO_2.

3.2. Reaction model based on hydrogen spillover

In this section, we discuss the mechanism of reactions between spilt-over hydrogen and NO_x adsorbates stored on the surface of MnO_x–CeO_2, which take place in the presence of Pd. The two possible models for this NO_x–H_2 reaction can be proposed. The first model is the reaction between gaseous NO and the anion

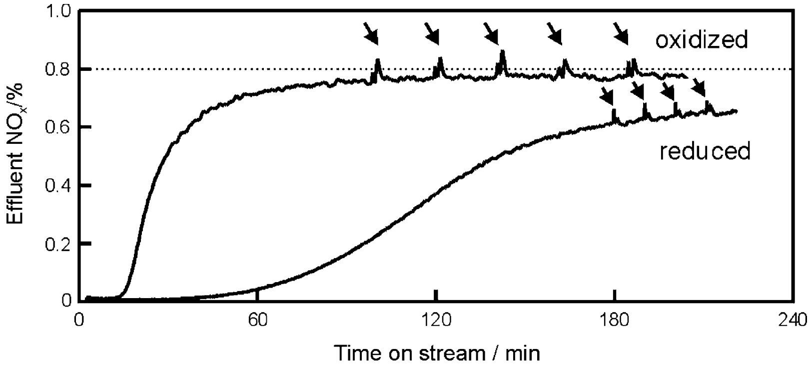

Fig. 3. Effect of H_2 pulses on effluent NO_x from MnO_x–CeO_2 at 150 °C. Each H_2 pulse was $1.0\,cm^3$; Gas feed: 0.08% NO, 2% O_2, He balance, $W/F = 0.24\,s\,g\,cm^{-3}$. The sample was treated at 400 °C in a flowing 10% O_2/He (oxidized) or 5% H_2/He (reduced) before use.

vacancy created by spilt-over hydrogen. To ascertain this process, unloaded MnO_x–CeO_2 samples after pretreatment in a stream of 10% O_2/He or 5% H_2/He at 400 °C were placed in a stream of 0.08% NO/He at 150 °C with monitoring the NO_x concentration in the effluent gas (Fig. 3). For the sample oxidized in 10% O_2/He, the apparent breakthrough was observed after ca. 15 min, compared to ca. 60 min that was required for the reduced sample. Simple adsorptive NO removal was solely observed over the oxidized MnO_x–CeO_2, whereas much N_2 was evolved from the reduced sample. The difference of breakthrough curves is therefore due to the occurrence of NO reduction over reduced MnO_x–CeO_2. In the present system, MnO_x–CeO_2 is composed of a fluorite-type solid solution, where the redox of Mn ions is accompanied by reversible formation of oxygen vacancies [8]. The result of the present study evidences that these oxygen vacancies play a role of the reducing agent for NO_x adsorbed on the oxide surface even in the absence of Pd catalyst.

On approaching the saturation of NO sorption in Fig. 3, the microinjection of $1\,cm^3$ H_2 was repeated, but significant response was not detected. This means that MnO_x–CeO_2 cannot be reduced without the assistance of Pd at 150 °C, because the reduction should be brought about by the hydrogen spillover. Because of the higher reactivity of atomic hydrogen compared to molecular hydrogen, the reduction of several metal oxide systems has been reported to be promoted by the occurrence of hydrogen spillover [14].

The second model is based on the direct reduction of NO_x adsorbates by spilt-over hydrogen. This process can be detected by introducing H_2 to NO_x-adsorbed Pd/MnO_x–CeO_2 at 150 °C as shown in Fig. 4. After breakthrough of the NO adsorption and subsequent flush with He, the supply of a 5% H_2/He flow caused a very large N_2 evolution, which corresponds to the amount of NO_x adsorbed on MnO_x–CeO_2. To explain this result, the direct reaction between the NO_x adsorbates and spilt-over hydrogen must be taken into consideration. This process requires continuous H_2 supply to NO_x-saturated MnO_x–CeO_2, which would expand the reduced area on the surface of MnO_x–CeO_2 and consequently convert a large number of NO_x adsorbates into N_2.

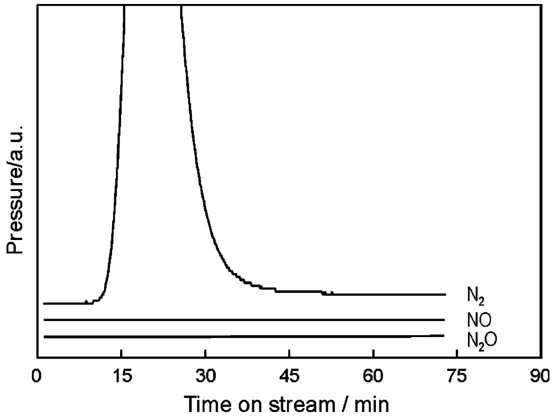

Fig. 4. Concentration profiles of effluent from NO_x-adsorbed 1 wt.% Pd/MnO_x–CeO_2 in flowing 5% H_2/He at 150 °C.

These results clearly support that the two processes described above were responsible for the NO_x–H_2 reactions over Pd/MnO_x–CeO_2 catalyst. In the presence of excess O_2, however, the reduction of NO_x is suppressed because of competitive H_2–O_2 combustion over Pd. According to our previous work [9], the non-selective character of Pd for NO–H_2 reaction can be improved by using NO_x-adsorbing material as a support. However, the dramatic effect cannot be expected at low H_2 concentration (<1%) in excess O_2 (10%). Furthermore, higher O_2 concentration causes the conversion of NO_x adsorbates from nitrite to nitrate that is less reactive toward hydrogen [11]. These considerations suggest that the NSR cycle, a process alternating sorptive NO_x removal and subsequent reduction by lean H_2, would be more suitable for the present catalyst system.

3.3. NSR cycles

The NSR cycles were next conducted by alternating two gas feeds, i.e. 0.080% NO, 10% O_2, balanced by He for a storage step and 1% H_2 balanced by He for a reduction step. The cycle time was set to 12 min for all the experiment. Fig. 5a shows the change of effluent NO_x concentration during the NSR cycles at 125 °C. In the storage step denoted as “S” (9 min), NO in the gas feed was removed by oxidative adsorption onto MnO_x–CeO_2. On approaching the saturation of NO uptake, this was followed by the reduction step denoted as “R”, where the gas feed was switched to H_2/He for 9 min. The hydrogen was consumed to bring about the reduction of NO_x adsorbates to N_2 and thus regenerate the adsorbability. When the “S” and “R” periods were changed to 10 and 2 min, respectively,

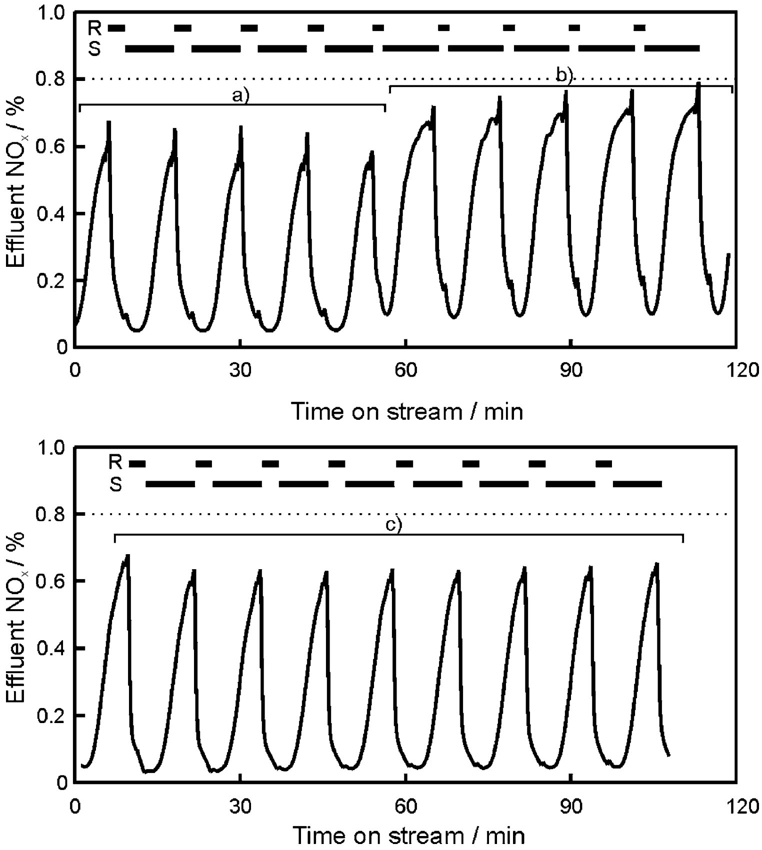

Fig. 5. NSR cycles over 1 wt.% Pd/MnO_x–CeO_2 at 125 °C: (a) S—0.08% NO, 10% O_2, He balance, 9 min; R—1% H_2/He, 3 min; (b) S—0.08% NO, 10% O_2, He balance, 10 min; R—1% H_2/He, 2 min; (c) S—0.08% NO, 5% O_2, He balance, 9 min; R—1% H_2/He, 3 min; $W/F = 0.24\,s\,g\,cm^{-3}$.

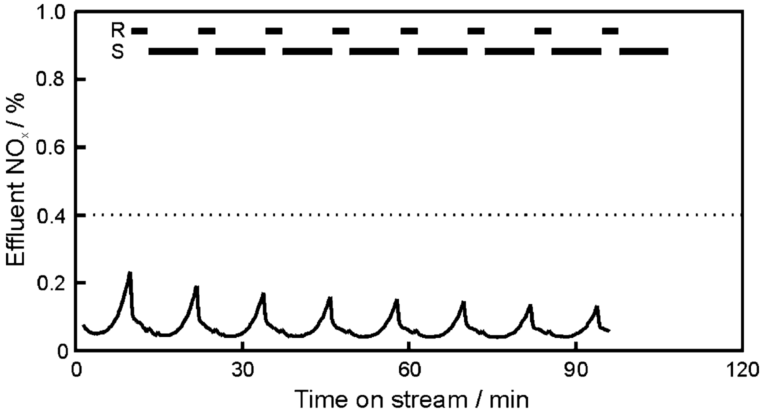

Fig. 6. NSR cycles over 1 wt.% Pd/MnO$_x$–CeO$_2$ at 125 °C: S—0.04% NO, 5% O$_2$, He balance, 9 min; R—1% H$_2$/He, 3 min; W/F = 0.24 s g cm^{-3}.

Table 1
Comparison of NSR cycle and steady state NO–H$_2$–O$_2$ reaction

Reaction mode	Average concentration in gas feed			Average conversion of NO[a] (%)
	NO (%)	H$_2$ (%)	O$_2$ (%)	
NSR[b] S: 10 min, R: 2 min	0.067	0.17	8.3	50
S: 9 min, R: 3 min	0.055	0.25	7.5	69
SSR[c]	0.080	0.28	10	4
	0.080	1.0	10	11
	0.080	2.0	10	59

[a] Conversion to N$_2$/N$_2$O.
[b] S—0.080% NO, 10% O$_2$, He balance, W/F = 0.24 s g cm^{-3}; R—1% H$_2$, He balance, W/F = 0.24 s g cm^{-3}.
[c] W/F = 0.24 s g cm^{-3}.

the observed NO$_x$ concentration increased (Fig. 5b). Fig. 5c exhibits the results obtained for NO adsorption in the presence of 5% O$_2$. Compared with Fig. 5a, the concentration of excess O$_2$ in the storage step seems to cause negligible effects on the efficiency of NO$_x$ reduction. Fig. 6 exhibits the result for inlet NO concentration at 0.04%. Because of limited NO$_x$ removal capacity of MnO$_x$–CeO$_2$, total removal of NO$_x$ was improved with a decrease of inlet NO$_x$ concentration. The large capacity of NO$_x$ sorption is thus one important factor for the efficient NO$_x$ reduction by the NSR cycles.

It is useful to compare the NSR cycles and conventional steady state reactions (SSR) in a stream of NO–H$_2$–O$_2$ (Table 1). The SSR was carried out in a stream of 0.08% NO, 0.28–2% H$_2$, 10% O$_2$ and He balance at the same temperature (150 °C). In this case, the supply of H$_2$ at least 2% in the gas feed is necessary for a considerable NO conversion. This is clear indication of nonselective character of Pd catalysts for NO–H$_2$ reactions in an oxidizing atmosphere. Nevertheless, the present study has demonstrated the selectivity can be much improved by applying the NSR cycle to Pd/MnO$_x$–CeO$_2$. The NSR results shown in Table 1 with average concentration of 0.055% NO, 0.25% H$_2$, 7.5% O$_2$ and He balance, attained much higher NO conversion of 69%, compared to only 4% for the conventional SSR mode. The noticeable difference of deNO$_x$ efficiency suggests that the combination of Pd and the NO$_x$-sorbing material, MnO$_x$–CeO$_2$, is a useful design for the low temperature NSR catalyst.

4. Conclusion

The catalyst combining Pd and NO_x-sorbing material, MnO_x–CeO_2, was found to be effective for NSR by H_2 at low temperatures. The oxidative NO adsorption onto MnO_x–CeO_2 yields nitrate and nitrite species, which are reduced by hydrogen spilt-over from Pd. The spilt-over hydrogen immediately gives rise to the anion vacancy on the surface of MnO_x–CeO_2, which plays as a reducing agent for NO. Also, the spilt-over hydrogen can directly reduce the nitrate/nitrite species covering the surface of MnO_x–CeO_2. However, the reduction of NO_x is inhibited by excess O_2, because of competitive H_2–O_2 reactions and conversion of nitrite to nitrate less reactive toward hydrogen. To avoid this problem, the NSR cycle, a process alternating sorptive NO_x removal and subsequent reduction by lean H_2, was applied to the present system. The NSR cycle was found to exhibit the efficient NO conversion at low H_2 consumption rate, which cannot be achieved by conventional steady state NO–H_2–O_2 reaction.

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