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Article

Promoting NO_x reduction via *in situ* activation of perovskite supported Pd catalysts under alternating lean-burn/fuel-rich operating atmospheres

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ABSTRACT

Herein, we report the excellent De-NO_x performance of La_{0.7}Sr_{0.3}MnO₃ (LSM) perovskite-supported Pd catalysts (Pd-LSM) in alternating lean-burn/fuel-rich atmospheres using C₃H₆ as reductant and describe the *in situ* activation of the Pd catalysts via metal-support interaction (MSI) tuning. The NO_x reduction conversion of the Pd-LSM catalyst increased significantly from 56.1% to 90.1% and the production of N₂O was suppressed. Our results demonstrated that this behavior was mainly attributed to the *in situ* transformation of Pd²⁺ into Pd⁰ during the reaction. The generated Pd⁰ species could readily activate the C₃H₆ reductant and achieve an eight-fold higher turnover frequency than Pd²⁺ for the reduction of NO_x. Moreover, excessive MSIs inhibited the *in situ* generation of Pd⁰, and thereby, lowered the De-NO_x activity of the catalyst even at high Pd dispersion. In addition, the Pd-LSM catalysts exhibited much higher S tolerance than conventional Al₂O₃-supported catalysts. Our study provides a new approach for analyzing and designing highly active metal catalysts operated under dynamic alternating oxidizing/reducing atmospheric conditions.

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1. Introduction

Lean-burn engines are widely used owing to their advantages, including good fuel economy and low CO₂ emissions [1–3]. However, nitrogen oxides (NO_x), including NO and NO₂, exhausted from lean-burn engines cannot be effectively purified using traditional three-way catalysts in the presence of excess O₂ [4–6]. Toyota company performed extensive studies and proposed the NO_x storage and reduction (NSR) technique,

which involves the use of lean-burn NO_x traps as a suitable approach for the elimination of NO_x [7,8]. NSR catalysis can be described as successively alternating lean-burn/fuel-rich cycles, which switch between a relatively long lean-burn period, during which NO is oxidized to NO₂ and then stored as nitrites/nitrates on the basic components of the catalysts, and a subsequent short fuel-rich pulse, during which the stored NO_x is released and reduced to harmless N₂ [9–11].

ABO₃ perovskites, which have been investigated as substi-

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tutes of conventional Pt-based catalysts, are promising NSR materials [12,13]. In particular, perovskites with La as the A-site metal exhibited excellent oxidation ability, high thermal stability, and flexible tunability [14–22]. The partial substitution of Sr at the A-sites could further increase the NO oxidation and NO_x trapping abilities of perovskites [23]. Mn is one of the most commonly used perovskite B-site metals for NSR applications, owing to its high stability under reducing atmosphere [23]. Li et al. [23] reported that the La_{0.9}Sr_{0.1}MnO₃ perovskite maintained its structural integrity after H₂ reduction. The strong tolerance of Mn-based perovskites to reducing atmospheres confers them high durability during the alternating lean-burn/fuel-rich NSR process, and thereby improves their prospects in industrial applications.

However, the low NO_x reduction ability of perovskites under fuel-rich atmospheres has limited their industrial applications [24], and therefore, the addition of Pd to perovskites was considered to be a possible solution for this drawback [12,13]. The activation temperature of reductants over Pd-based catalysts is lower than over those of Pt- and Rh-based catalysts; moreover, Pd-based catalysts present high-temperature durability and prominent De-NO_x activity [25–28]. Therefore, Pd is a critical component of De-NO_x catalysts. However, Pd presents low NO oxidation ability [29,30], which limits its NO_x trapping efficiency during NSR reactions. González-Velasco [31] reported that the addition of perovskites to Pd could overcome the shortcomings of Pd as NO oxidation catalyst. Even though Pd has been extensively used for De-NO_x reactions, the active chemical states of the Pd sites, i.e. Pd metal or oxide, has not been elucidated so far [32–34]. Liu et al. reported that PdO was active for the H₂-selective catalytic reduction reaction [33]. Conversely, Hu et al. [34] determined that the high oxidation state of Pd in PdO contributed to its low De-NO_x activity during three-way catalysis. It is difficult to identify the active sites of Pd catalysts during the NSR reaction because of the successively alternating lean-burn/fuel-rich cycling. Metal-support interactions (MSIs) can change the electronic states of Pd species [25,34–36]. Therefore, MSI tuning is an effective way to obtain Pd sites with different chemical states, and that provides direct evidence for the identification of the active Pd species and important information for the development of highly active Pd catalysts for De-NO_x using the NSR technique.

In this study, we designed and synthesized perovskite (La_{0.7}Sr_{0.3}MnO₃)-supported Pd catalysts with different Pd-perovskite interactions. We determined that during the NSR reaction the Pd species underwent *in situ* activation from PdO to metallic Pd, and that greatly enhanced the De-NO_x activity of the catalyst, which presented outstanding tolerance to H₂O, CO₂, and SO₂. Moreover, it was confirmed that this behavior strongly depended on the strength of the Pd-perovskite interactions. Furthermore, we used kinetic measurements to determine that the turnover frequency (TOF) for the reduction of NO_x on Pd⁰ sites was eight-fold higher than that on Pd²⁺ sites. These findings provided deep insight into the active Pd species during the NSR reaction and new perspectives for the design of efficient catalysts operated under dynamic alternating oxidizing/reducing atmospheric conditions.

2. Experimental

2.1. Preparation of the catalysts

The Pd-free La_{0.7}Sr_{0.3}MnO₃ catalyst was prepared using the sol-gel method and was denoted as LSM. Stoichiometric amounts of La(NO₃)₃·6H₂O, Sr(NO₃)₂, Mn(NO₃)₂, citric acid (CA) and ethylene diamine tetraacetic acid (EDTA) (which were supplied by Aladdin Industrial Corporation) were added to 300 mL deionized water, and the molar ratio of metal cations:CA:EDTA was maintained at 1:1:1.5. The solvent water was subsequently evaporated via stirring at 80 °C and at pH 7 until a viscous gel formed. Thereafter, the obtained gel was dehydrated in a vacuum oven at 80 °C for 12 h followed by two-step calcination in a muffle furnace at 300 °C for 2 h and under air flow at 700 °C for 6 h. The calcined La_{0.7}Sr_{0.3}MnO₃ was used as catalyst and precursor for the subsequent impregnation process.

The sol-gel prepared Pd-containing La_{0.7}Sr_{0.3}MnO₃ catalyst (Pd-LSM-SG) was obtained using a same protocol utilized for the preparation of LSM. Pd(NO₃)₂·2H₂O (Aladdin Industrial Corporation) was added to the aforementioned mixture of nitrates.

Another Pd-containing La_{0.7}Sr_{0.3}MnO₃ catalyst was prepared via the wet-impregnation method (Pd-LSM-IM), and the prepared La_{0.7}Sr_{0.3}MnO₃ precursor served as Pd support. The impregnated catalyst was dried in an oven at 120 °C for 10 h, and then it was calcined at 500 °C for 4 h under air flow. The Pd loadings of the Pd-LSM-SG and Pd-LSM-IM catalysts were confirmed to be 2.1 wt% using a Vista MPX inductively coupled plasma atomic emission spectroscopy instrument.

Conventional Pt/BaO/Al₂O₃ and Pd/BaO/Al₂O₃ catalysts with the same noble metal weight loadings were prepared as reference using the two-step wet-impregnation method [37,38].

2.2. Characterizations of the catalysts

The specific surface areas (SSAs) of the catalysts were measured via the N₂ physisorption method at –196 °C using a QuadraSorb SI (Quantachrome) instrument.

X-ray diffraction (XRD) experiments were performed on an X'pert Pro (PANalytical) diffractometer with Cu K_α (λ = 0.15418 nm) radiation source at a scanning speed of 0.083° s^{–1} and step size of 0.02°.

X-ray absorption fine structure (XAFS) measurements were carried out at the 14W1 and 1W1B beamlines of the Shanghai and Beijing Synchrotron Radiation Facilities, respectively, in transmission mode. The radial structure functions of the Pd K-edge were obtained after Fourier transformation.

X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI-1600 ESCA (Manufacturer) spectrometer with Mg K_α (1253.6 eV) radiation at a pressure of 5 × 10^{–8} Pa, scanning speed of 1 eV s^{–1}, and step size of 0.05 eV.

H₂ temperature programmed reduction (H₂-TPR) tests were performed using 30 mg of catalyst powder utilizing a TPDRO (TP-5080, Xianquan Co.) multi-automatic characterization ad-

sorption instrument equipped with a thermal conductivity detector. Prior to the tests, the catalysts were pretreated under N_2 flow at 500 °C for 30 min to remove the absorbed species. After the catalysts were cooled to room temperature under N_2 atmosphere, they were heated under a 8% H_2/N_2 flow at a rate of 30 mL min^{-1} and at a heating ramp of 10 °C min^{-1} .

C_3H_6 oxidation tests were performed in a fixed-bed reactor loaded with 100 mg catalyst. The feeding gas was a mixture of 1000 ppm C_3H_6 and 2% O_2 in N_2 (200 mL min^{-1}), and the space velocity was 120 000 mL $g^{-1} h^{-1}$. Prior to the tests, the catalysts were pretreated at 350 °C under a N_2 flow to remove the adsorbed CO_2 . The tests started at 150 °C at a heating rate of 2 °C min^{-1} . The generated CO_2 was detected using an EN-308 (Shanghai Encel Instruments Co.) infrared gas analyzer. The temperatures at which the C_3H_6 conversion reached 50% and 100% were denoted as T_{50} and T_{100} , respectively.

CO chemisorption measurements were performed to calculate the Pd dispersion. The catalysts were first reduced at 100 °C under a 1% CO/N_2 flow for 1 h and subsequently heated under a N_2 flow at 500 °C for 0.5 h to remove the adsorbed CO and CO_2 . After the catalysts were cooled to room temperature under a N_2 flow, they were exposed to a 800 ppm CO/N_2 flow for chemisorption measurements, and the outlet CO concentration was recorded using the infrared gas analyzer.

2.3. Catalytic activity and selectivity measurements

Alternating NSR experiments were performed in the temperature range of 250–450 °C by alternating between 50 s lean-burn and 10 s fuel-rich periods. First, 200 mg of catalyst particles (40–60 mesh) was loaded in the fixed-bed reactor. The NSR reaction reached steady state after 30–40 cycles. The performance of the catalysts during these cycles was analyzed and the obtained data were used to calculate the De- NO_x activities of the catalysts. The lean-burn gas mixture consisted of 400 ppm NO and 5% O_2 balanced with N_2 and the fuel-rich gas mixture comprised 1000 ppm C_3H_6 balanced with N_2 . A flow rate of 400 mL min^{-1} was maintained during the lean-burn and fuel-rich phases (space velocity of 120 000 mL $g^{-1} h^{-1}$). The main by-product in the exhaust was N_2O and its concentration was monitored using a N_2O S710 (SICK MAIHAK) modular gas analyzer. The detailed calculation methods for the NO_x storage efficiency, NO_x reducing efficiency, NO_x removal percentage (NRP), N_2O selectivity, and N_2 selectivity are included in the Supplementary Material.

Selectivity tests were performed over the catalysts (200 mg) at 350 °C. The catalysts were saturated with NO_x under the lean-burn atmosphere and were subsequently regenerated under the fuel-rich atmosphere (1000 ppm $C_3H_6/5\% H_2O/5\% CO_2/N_2$). The outlet signals of NO, NO_2 , N_2 , and C_3H_6 were recorded using an HPR 20 (Hiden Analytical) mass spectrometer during the regeneration period. The concentration of N_2O in the exhaust was detected using the N_2O modular gas analyzer. The feed compositions and space velocity were the same as those used for the NSR tests.

Low-temperature De- NO_x tests were performed in a fixed-bed reactor at 200 °C using 100 mg of catalysts to calcu-

late the TOFs of the catalysts. To eliminate the effects of the internal and external diffusion, the space velocity was maintained at 240 000 mL $g^{-1} h^{-1}$. First, the catalysts were exposed to the lean-burn atmosphere for 2 min to store NO_x . Subsequently, the feeding gas was switched to the fuel-rich atmosphere for the NO_x reduction reaction. The compositions and flow rates of the lean-burn and fuel-rich atmospheres were the same as those used for the catalytic activity tests. The conversion of C_3H_6 over the catalysts was controlled below 10% to maintain the reaction in the kinetic regime. The outlet concentrations of CO and CO_2 were monitored using the aforementioned infrared gas analyzer.

3. Results and discussion

3.1. Physicochemical properties of the catalysts

Fig. 1 presents the XRD patterns of the catalysts. The main diffraction peaks of the fresh LSM, Pd-LSM-SG, and Pd-LSM-IM catalysts matched well with those of the $La_{0.7}Sr_{0.3}MnO_3$ perovskite (JCPDS 54-1195), which confirmed the formation of the perovskite structure. The perovskite diffraction peaks of Pd-LSM-SG or Pd-LSM-IM did not shift or indicate crystalline structure changes owing to the addition of Pd to the $La_{0.7}Sr_{0.3}MnO_3$ perovskite, which demonstrated that Pd did not enter the perovskite lattice. Similar findings were reported in the literature and were ascribed to the mismatch between the ionic radii of $Pd^{3+/4+}$ and Mn^{3+} [39]. The weak peak at 33.90° in the XRD pattern of the Pd-LSM-SG catalyst, which was attributed to the PdO phase (JCPDS 41-1107), was absent from the XRD pattern of the Pd-LSM-IM catalyst. This indicated that the grain size of the Pd-containing phase of the Pd-LSM-IM catalyst was below the XRD detection limit. The SSAs of the catalysts are summarized in Table 1 and their values were similar (approximately 14 m² g^{-1}).

We used the XAFS technique to further investigate the valence and local coordination environment of the Pd species in the catalysts. Fig. 2 illustrates the X-ray absorption near-edge structure (XANES) spectra of Pd K-edge and radial distribution

Fig. 1. XRD patterns of the fresh $La_{0.7}Sr_{0.3}MnO_3$ (1), fresh sol-gel-prepared $La_{0.7}Sr_{0.3}MnO_3$ -supported Pd (2), and fresh wet-impregnation-prepared $La_{0.7}Sr_{0.3}MnO_3$ -supported Pd (3) catalysts.

Table 1Physicochemical properties and De-NO_x activities of the catalysts at 350 °C.

Catalyst	Pd content ^a (wt%)	Specific surface area (m ² g ⁻¹)	NO _x storage efficiency ^b (%)	NO _x reducing efficiency ^b (%)	NO _x removal percentage ^b (%)	N ₂ O selectivity ^c (%)
LSM ^d	—	14.3	59.0	58.3	34.4	2.7
Pd-LSM-SG ^e	2.1	14.9	98.9	91.1	90.1	2.6
Pd-LSM-IM ^f	2.1	13.4	97.2	74.0	72.0	5.0

^a Determined via inductively coupled plasma optical emission spectroscopy^b Determined using the data in Fig. S3^c Determined using the data in Fig. S4^d Pure La_{0.7}Sr_{0.3}MnO₃^e Sol-gel-prepared La_{0.7}Sr_{0.3}MnO₃-supported Pd^f Wet-impregnation-prepared La_{0.7}Sr_{0.3}MnO₃-supported Pd

function (RDF) profiles of the fresh catalysts. The XANES spectra of the Pd-LSM-SG and Pd-LSM-IM catalysts highly resembled that of the PdO standard sample (Fig. 2(a)). This suggested that the Pd species in the Pd-LSM-SG and Pd-LSM-IM catalysts mainly existed as PdO. The doublet at the white line, which was attributed to the lattice Pd cations [39], was not observed in the XANES spectra of the Pd-LSM-SG and Pd-LSM-IM catalysts in this study. This indicated that no lattice Pd species (Pd^{3+/4+}) were present in the catalysts. Only one major coordination shell centered at approximately 0.24 nm, which was ascribed to the first Pd-Pd coordination shell of metallic Pd, was observed in the RDF profile of Pd foil [40]. The reference PdO sample presented two coordination shells at approximately 0.15 and 0.29 nm, which were ascribed to the first Pd-O and Pd-Pd coordination shells, respectively [12,28]. The coordination shells of the Pd-LSM-SG and Pd-LSM-IM catalysts were located at similar positions and therefore, confirmed that the Pd species were present as PdO.

The difference in intensity between the Pd-Pd coordination shells of the fresh Pd-LSM-SG and Pd-LSM-IM catalysts offered insights into the Pd dispersion. The intensity of the Pd-Pd shell in the XANES spectra of the Pd-LSM-SG catalyst was comparable with that of the PdO standard sample and that of the Pd-LSM-IM was weaker. The differences in the intensities of the

Pd-O shells of the three catalysts were negligible. The weak intensity of the Pd-Pd shell of the Pd-LSM-IM catalyst could be attributed to the crystallite size and dispersion of PdO on the La_{0.7}Sr_{0.3}MnO₃ surface being smaller and higher, respectively, than that of the Pd-LSM-SG catalyst [41]. These results were in good agreement with the absence of the 33.90° PdO peak from the XRD profile of the fresh Pd-LSM-IM catalyst (Fig. 1).

The high-resolution transmission electron microscopy (HRTEM) images of the fresh Pd-LSM-SG and Pd-LSM-IM catalysts were used to characterize the morphology of the La_{0.7}Sr_{0.3}MnO₃ support and determine the PdO particle size (Fig. S1). Spherical 20–40 nm perovskite particles were observed in the HRTEM images of both catalysts and a thin amorphous layer was wrapped around the perovskite particles. The surface elemental analysis results in Table S1 revealed that the surface Sr/La atomic ratios of the fresh catalysts were much higher than the stoichiometric ratio (0.43), which suggested that the amorphous layer consisted of Sr species. We combined our results with those reported in the literature [42,43], and ascribed the amorphous layer to the surface enrichment in SrCO₃. The HRTEM images revealed that the PdO particles in the Pd-LSM-IM catalyst were relatively small (3–5 nm) and dispersed on the surface of the perovskite. This explained the absence of the PdO phase from the XRD pattern of the Pd-LSM-IM catalyst (Fig. 1). For the Pd-LSM-SG catalyst, owing to the sol-gel preparation process, the PdO particles were partially embedded in the perovskite bulk rather than dispersed on the perovskite surface. Moreover, the contrast between the Pd and perovskite phases in the HRTEM image of the Pd-LSM-SG catalyst was relatively poor, and therefore, the images could not be used to identify the presence of the PdO phase in the Pd-LSM-SG catalyst.

Fig. 3 depicts the XPS profiles of the fresh catalysts. The binding energy (BE) of the Pd 3d_{5/2} core level of the Pd-LSM-SG catalyst was centered at 336.7 eV, which was ascribed to Pd²⁺ (336.1–336.9 eV) (Fig. 3(a)) [31,44]. In comparison, the BE peak of Pd 3d_{5/2} of the Pd-LSM-IM catalyst was centered at 337.1 eV, which was upshifted by 0.4 eV. This suggested that the interactions between the PdO particles and perovskite in the Pd-LSM-IM catalyst were stronger than those in the Pd-LSM-SG catalyst [13]. González-Velasco recently reported similar findings and also demonstrated that the wet-impregnation preparation method resulted in stronger Pd-perovskite interactions than the sol-gel method [31]. More-

Fig. 2. Normalized Pd K-edge X-ray absorption near-edge structure spectra (a) and radial distribution function profiles (b) of the Pd-foil (1) PdO (2), fresh sol-gel-prepared La_{0.7}Sr_{0.3}MnO₃-supported Pd (3), and fresh wet-impregnation-prepared La_{0.7}Sr_{0.3}MnO₃-supported Pd (4) catalysts.

Fig. 3. Pd 3d (a) and Mn 2p (b) XPS profiles of the fresh sol-gel-prepared $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ -supported Pd (1) and fresh wet-impregnation-prepared $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ -supported Pd (2) catalysts.

over, the Pd 3d XPS peak intensities of the Pd-LSM-IM catalyst were much stronger than those of the Pd-LSM-SG catalyst. This was ascribed to the impregnated Pd species being highly dispersed on the surface of the Pd-LSM-IM catalyst, whereas a fraction of Pd was embedded in the perovskite bulk for the Pd-LSM-SG catalyst. These findings were in good agreement with the HRTEM results.

Fig. 3(b) depicts the Mn 2p XPS spectra of the Pd-LSM-IM and Pd-LSM-SG catalysts. The Mn 2p XPS spectra could be deconvoluted into six peaks, which corresponded to Mn^{3+} (641.7 and 653.3 eV), Mn^{4+} (643.0 and 654.6 eV), and their satellite peaks (644.6 and 656.2 eV). These results demonstrated the coexistence of Mn^{3+} and Mn^{4+} cations on the surface of the $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ perovskite, as summarized in Table 2. Furthermore, we determined that Mn^{4+} accounted for 42.6% and 33.5% of the Mn species in the fresh Pd-LSM-SG and

Pd-LSM-IM catalysts, respectively. We hypothesized that owing to the strong MSI, electrons could have transferred from the Pd cations to the surface Mn cations in the Pd-LSM-IM catalyst; however, other factors might have been involved in the electron transfer process.

The H_2 -TPR profiles of the fresh catalysts (Fig. 4(a)) were used to illustrate the interactions between the perovskite and Pd species. The Pd-free LSM catalyst presented two H_2 consumption peaks at 449 and 709 °C (Fig. 4(a)), which were ascribed to the reduction of Mn^{4+} to Mn^{3+} and Mn^{3+} to Mn^{2+} , respectively [28,45]. The reduction temperatures of the Pd-LSM-SG and Pd-LSM-IM catalysts of 260 and 135 °C, respectively, were much lower than those of the LSM catalyst. The significant temperature shift of the Mn^{4+} reduction peak was caused by the H_2 spillover from metallic Pd to perovskite.

A narrow intense peak centered at 80 °C, which corre-

Table 2

Chemical states of the Pd and Mn species in the fresh and activated catalysts determined from the XANES and XPS results.

Catalyst	XANES		XPS			
	Pd^0 (%)	Pd^{2+} (%)	Pd^0 (%)	Pd^{2+} (%)	Mn^{3+} (%)	Mn^{4+} (%)
Fresh Pd-LSM-SG	100	0	100	0	57.4	42.6
Fresh Pd-LSM-IM	100	0	100	0	66.5	33.5
Activated Pd-LSM-SG	53.0	47.0	43.6	56.4	58.0	42.0
Activated Pd-LSM-IM	6.0	94.0	0	100	67.1	32.9

Fig. 4. H_2 -TPR profiles (a) and magnified area marked with a dashed square (b) in (a). (1) PdO; (2) fresh pure $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$; (3) fresh sol-gel-prepared $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ -supported Pd; (4) fresh wet-impregnation-prepared $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ -supported Pd catalysts.

sponded to the reduction of Pd^{2+} to Pd^0 , was observed in the H_2 -TPR profile of the reference PdO sample. Consequently, the reduction peak centered at 110°C in the H_2 -TPR profile of the Pd -LSM-SG catalyst could be ascribed to the combined reduction of Pd^{2+} and a small amount of Mn^{4+} cations adjacent to Pd species. Most Mn^{4+} cations were less influenced by the H_2 spillover effect and were reduced at higher temperatures, which corresponded to the peak centered at 260°C . Similar, no segregated reduction peak for the Pd species was observed in the H_2 -TPR profile of the Pd -LSM-IM catalyst. The sharp reduction peak at 135°C in the H_2 -TPR profile of the Pd -LSM-IM catalyst was attributed to the reduction of both Pd^{2+} and Mn^{4+} . The impregnated Pd in the Pd -LSM-IM sample induced an even more pronounced H_2 spillover effect because all Mn^{4+} cations were reduced before 200°C , which confirmed that PdO in the Pd -LSM-IM catalyst was highly dispersed on the perovskite surface.

The H_2 -TPR profiles of the catalysts in the temperature range of 40 – 170°C were magnified and presented in Fig. 4(b). Although the reduction peaks of Pd^{2+} and Mn^{4+} of the catalysts overlapped, Pd^{2+} was reduced before Mn^{4+} . Owing to the MSI, for the Pd -LSM-SG catalyst, the reduction of Pd^{2+} started at 61°C , which exceeded the temperature required for the PdO sample (28°C). The reducibility of Pd^{2+} for the Pd -LSM-IM catalyst was even lower than that for the Pd -LSM-SG catalyst, as indicated by the higher initial reduction temperature of 84°C . This indicated that the interactions between perovskite and the small PdO particles for the Pd -LSM-IM catalyst were stronger than those between perovskite and the larger PdO particles for the Pd -LSM-SG catalyst, which was in accordance with the XPS results in Fig. 3.

3.2. Catalytic activity of the catalysts

To elucidate the effect of the Pd -perovskite interactions on the NSR performance of the catalysts, we measured the De- NO_x activities of the catalysts in the temperature range of 200 – 450°C , and the results are presented in Fig. 5(a). The temperature evolution of the De- NO_x activities of the three catalysts pre-

sented a volcanic shape, and the maximum activities were observed at 350°C . The LSM catalyst presented low NO_x removal efficiency, owing to the limited NO_x reduction ability of LSM during the fuel-rich periods [12,42]. The De- NO_x activities of the Pd -containing catalysts were significantly higher than those of the Pd -free catalyst over the entire temperature range. The NRPs of the catalysts decreased as follows: Pd -LSM-SG > Pd -LSM-IM > LSM. Fig. S2 presents the N_2 selectivity of the catalysts in the temperature range of 200 – 450°C . Typically, a small amount of NH_3 is generated when C_3H_6 is used as the reductant [46]. Thus, N_2O was the main by-product of the NSR reactions. The catalysts presented remarkable N_2 selectivity, which exceeded 90% above 350°C (Fig. S2). However, the N_2O selectivity of the catalysts increased by approximately 20% with decreasing the reaction temperature to 200 or 250°C . The Pd -LSM-SG catalyst presented higher N_2 selectivity than the Pd -LSM-IM catalyst over the entire temperature range.

To further compare the catalytic activities of the Pd -containing catalysts, we obtained the outlet NO_x , CO_2 , and N_2O evolution curves during lean-burn/fuel-rich cycling at 350°C , and the results are presented in Figs. S3 and S4 and Table 1. The Pd -LSM-SG and Pd -LSM-IM catalysts presented excellent NO_x trapping performance during the lean-burn periods (Fig. S3). However, the Pd -LSM-SG catalyst reduced more NO_x than the Pd -LSM-IM catalyst during the fuel-rich periods, and thus achieved a higher NRP.

The two Pd -containing catalysts with similar compositions but different degrees of MSI presented remarkably different activity trends. The NO_x evolution curve of the Pd -LSM-SG in Fig. S3(a) indicates that the catalyst experienced *in situ* activation during the initial alternating lean-burn/fuel-rich cycle. The amount of NO_x slip under reducing atmosphere gradually decreased (Fig. S3(a)), and that was accompanied by an increase in the CO_2 signals (Fig. S3(c)). This indicated that a continuously increasing amount of C_3H_6 participated in the NO_x reduction reaction. The De- NO_x activity of the Pd -LSM-SG catalyst was substantially increased as the NSR process proceeded. Fig. 5(b) presents the time evolution of the De- NO_x activities of the catalysts at 350°C wherein, the *in situ* activation behavior of the

Fig. 5. (a) De- NO_x activity of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ (LSM) (1), sol-gel-prepared $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ -supported Pd (Pd -LSM-SG) (2), and wet-impregnation-prepared $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ -supported Pd (Pd -LSM-IM) (3) at 200 – 450°C . (b) Time evolution of the De- NO_x activity of LSM (1), Pd -LSM-SG (2), Pd -LSM-IM (3), and pretreated Pd -LSM-SG (4) at 350°C . Reaction conditions: lean-burn phase: 50 s, 400 ppm $\text{NO}/5\% \text{O}_2/\text{N}_2$; fuel-rich phase: 10 s, 1000 ppm $\text{C}_3\text{H}_6/\text{N}_2$; space velocity: $120\,000 \text{ mL g}^{-1} \text{ h}^{-1}$.

catalysts can be distinctly observed. Approximately 25 cycles were necessary for the Pd-LSM-SG catalyst to reach steady state, during which, the NRP increased from 56.1% to 90.1%. Conversely, the NRP of the Pd-LSM-IM catalyst decreased from 81.0% to 72.0% when the reaction reached steady state after 25 cycles. These results demonstrated that the Pd-perovskite interactions played a crucial role in the De-NO_x performance of the catalysts. For the LSM catalyst, the occupied NO_x storage sites under lean-burn atmospheres could not be effectively regenerated under fuel-rich atmospheres owing to the absence of Pd [13], and therefore, the NRP of the LSM catalyst was low (34.2%; Fig. 5(b)). The perovskite-supported Pd catalysts were stable under redox switching atmosphere. No significant decrease in De-NO_x activity was observed for either the Pd-LSM-SG or Pd-LSM-IM catalysts after 10 h of reaction (Fig. S5).

To investigate the *in situ* activation behavior of the Pd-LSM-SG catalyst, we subjected it to 25 alternating NO_x-free lean-burn (5% O₂/N₂)/fuel-rich (1000 ppm C₃H₆/N₂) cycles prior to the NSR test. The activity trend of the pretreated Pd-LSM-SG catalyst was different than that of the fresh Pd-LSM-SG catalyst (Fig. 5(b)). The pretreated Pd-LSM-SG catalyst did not present *in situ* activation behavior and its NRP exceeded 90% during the entire NSR test. The activity of the pretreated Pd-LSM-SG catalyst was similar to that of the *in situ* activated Pd-LSM-SG catalyst. This suggested that the *in situ* activation process was completed during the pretreatment. Considering the pretreatment conditions, we concluded that the activation of the catalyst was not affected by NO_x.

3.3. Analysis of the Pd species on the activated catalysts

To further explore the origin of the *in situ* activation behavior of the catalysts, we analyzed their XRD and XAFS profiles. Hereafter, “activated catalysts” denote catalysts that were treated under a NSR reaction atmosphere until they achieved

stable activity. Fig. S6 presents the XRD patterns of the fresh and activated catalysts. The changes in peak positions and crystallinity of the perovskite phases of the catalysts after NSR activation were negligible, and this indicated that the Mn-based perovskite presented high structural stability under NSR conditions. The structural stability was further confirmed using the Mn 2p XPS profiles of the activated catalysts (Fig. S7), which revealed that the Mn oxidation state did not change significantly during the reaction. The intensity of the PdO diffraction peak of the Pd-LSM-SG catalyst decreased significantly after activation (Fig. 6(a)). Considering that the full-width at half-maximum of the PdO diffraction peak did not change significantly, the decrease in peak intensity after activation might be attributed to the phase transformation of PdO. However, the XRD pattern of the Pd-LSM-IM catalyst did not change after activation.

To identify the precise chemical states of the Pd species in the activated catalysts, we analyzed their XANES (Fig. 6(b)) and RDF profiles (Fig. 6(c)) of the Pd K-edge. The absorption edge of the activated Pd-LSM-IM catalyst was similar to that of the PdO standard sample. However, a noticeable change was observed for the activated Pd-LSM-SG catalyst. A new feature appeared in the XANES profile of the activated Pd-LSM-SG catalyst at 24390 eV, which was similar to that observed in the profile of the Pd foil but presented lower intensity. Fig. S8 illustrates the linear combination fitting of the activated catalysts and Table 2 summarizes the results. The Pd species in the activated Pd-LSM-SG catalyst consisted of 53% metallic Pd and 47% PdO, which indicated that 53% of the PdO in the fresh Pd-LSM-SG catalyst was transformed into metallic Pd during the NSR reaction.

The RDF profile of the activated Pd-LSM-SG catalyst exhibited new features, which corresponded to the changes in its XANES spectrum. In addition to the weakened Pd-O and Pd-Pd coordination shells of PdO, a new metallic Pd-Pd coordination shell appeared in the RDF profile of the activated Pd-LSM-SG

Fig. 6. (a) XRD patterns of the fresh sol-gel-prepared Pd-LSM-SG (1), activated Pd-LSM-SG (2), fresh Pd-LSM-IM (3), and activated Pd-LSM-IM (4); Normalized Pd K-edge X-ray absorption near-edge structure spectra (b) and radial distribution functions (c) of Pd foil (1), PdO (2), activated Pd-LSM-SG (3), activated Pd-LSM-IM (4), and sample (3) oxidized under lean-burn atmosphere at 350 °C for 8 min (5).

catalyst (Fig. 6(c)). These findings confirmed the partial *in situ* reduction of PdO to metallic Pd in the Pd-LSM-SG catalyst during the NSR process. Furthermore, these results offered a reasonable explanation for the decrease in the intensity of the PdO diffraction peak of the activated Pd-LSM-SG catalyst (Fig. 6(a)). Unlike the XANES and RDF profiles of the Pd-LSM-SG catalyst, those of the activated Pd-LSM-IM catalyst were not different from those of the fresh Pd-LSM-IM catalyst. The percentage of Pd⁰ species in the activated Pd-LSM-IM catalyst was very small (Table 2). Combining these results with the De-NO_x activity data in Fig. 5(b), it was reasonable to expect that for the Pd-LSM-SG catalyst, the *in situ* activation behavior was due to the gradual transformation of PdO to metallic Pd during alternating lean-burn/fuel-rich cycling. However, the highly dispersed PdO in the Pd-LSM-IM catalyst could be hardly reduced during the short fuel-rich periods because of the relative low reducibility of the Pd species caused by the strong Pd-perovskite interactions. Therefore, although the initial oxidation states of the Pd species in the two fresh catalysts were highly similar, the final chemical states of Pd after stabilization under the reaction atmospheres were determined by the interactions between Pd and perovskite. The change in the metallic Pd-Pd shell of the activated Pd-LSM-SG catalyst was negligible after it was exposed to a 5% O₂/N₂ atmosphere at 350 °C for 8 min (Fig. 6(c)). This demonstrated that the metallic Pd that formed in the activated Pd-LSM-SG catalyst was stable under lean-burn atmosphere.

Furthermore, we investigated the oxidation states of the Pd species in the activated conventional Pd/BaO/Al₂O₃ catalysts and compared them with those of the perovskite-supported Pd catalysts. As presented in Fig. 7, PdO species were present on the Al₂O₃ support, which confirmed the strong MSI of the Pd/BaO/Al₂O₃ catalyst, as indicated by the surface oxidation state, which was higher than +2 [47]. We could not detect the formation of Pd⁰ species after the NSR reaction, and accordingly, the activated conventional Pd/BaO/Al₂O₃ catalyst did not exhibit *in situ* activation behavior during the NSR process (Fig. S9). However, after the catalyst was pretreated at 350 °C under a fuel-rich flow (1000 ppm C₃H₆/N₂) for 3 min, a few Pd⁰ spe-

Fig. 7. Pd 3d XPS profiles of fresh Pd/BaO/Al₂O₃ (1), activated Pd/BaO/Al₂O₃ (2), Pd/BaO/Al₂O₃ reduced in 1000 ppm C₃H₆/N₂ at 350 °C for 3 min (3), and sample (3) after five NO_x storage and reduction cycles (4).

cies were generated. However, the formed Pd⁰ was rapidly re-oxidized after only five NSR cycles. Therefore, the Pd⁰ generated on the Al₂O₃ support was not stable under alternating oxidizing/reducing atmospheres. The only explanation for this phenomenon was the strong MSI, which facilitated the oxidation of the Pd⁰ generated under the fuel-rich atmosphere during its exposure to the lean-burn atmosphere. Thus, we concluded that for the Pd-LSM-SG catalyst, appropriate MSIs were essential for achieving the *in situ* activation of Pd.

The formation of Pd⁰ is not facilitated during most NSR reactions because the long oxygen-rich and short fuel-rich atmospheric periods alternate. For example, in this study, the lean-burn atmosphere consisted of 5% O₂ and the duration of the lean-burn process was 50 s. Conversely, the fuel-rich atmosphere comprised only 1000 ppm C₃H₆ and the rich-fuel process lasted for 10 s. Pd²⁺ is more stable than Pd⁰ under these reaction conditions, as observed for the Pd/BaO/Al₂O₃ catalyst. To the best of our knowledge, no reports on the *in situ* activation behavior of Pd-based NSR catalysts have been published. By tuning the MSI, we successfully achieved the partial *in situ* reduction of PdO to more active metallic Pd species on the perovskite support during the alternating fuel-rich/lean-burn NSR process and achieved excellent De-NO_x performance.

3.4. Activation of C₃H₆ on Pd⁰

Fig. 8(a) displays the C₃H₆ oxidation profiles of the fresh and activated catalysts and Table S2 summarizes their *T*₅₀ and *T*₁₀₀ values. The Pd-containing perovskite catalysts were much more active than the LSM catalyst for the oxidation of C₃H₆, as indicated by the decrease in *T*₁₀₀ of the LSM catalyst from 453 to below 260 °C. The C₃H₆ oxidation activity of the fresh Pd-LSM-SG catalyst was similar to that of the fresh Pd-LSM-IM catalyst (Fig. 8(a)). The C₃H₆ oxidation performance of the Pd-LSM-SG catalyst was improved after activation, and its *T*₅₀ and *T*₁₀₀ decreased from 255 to 227 °C and from 262 to 237 °C, respectively. However, the C₃H₆ oxidation performances of the fresh and activated Pd-LSM-IM catalysts were virtually the same. This implied that the Pd⁰ species formed during the NSR process played a crucial role for the activation of C₃H₆ over the activated Pd-LSM-SG catalyst. According to a previous study, C₃H₆ could be effectively adsorbed and activated on the metallic Pd-Pd bridge sites via the formation of di-σ-bonded or π-bonded species [48]. Combining these results with those of the NSR tests, we concluded that the activation of C₃H₆ on Pd⁰ could promote the De-NO_x reaction during the fuel-rich phase.

Fig. 8(b) presents the low-temperature De-NO_x performance of the catalysts at 200 °C, and the data were used to calculate the TOF of the NO_x reduction by C₃H₆ per Pd atom. The reaction was maintained under kinetic regime; the internal and external diffusion effects were eliminated, as shown in Fig. S10, and the reaction rate at 10 s after switching to fuel-rich atmosphere was used for TOF calculations. The activities of the catalysts decreased as follows: activated Pd-LSM-SG > activated Pd-LSM-IM ≈ fresh Pd-LSM-IM > fresh Pd-LSM-SG. For the Pd-LSM-SG catalyst, the formation of Pd⁰ after the *in situ* activation process significantly accelerated the NO_x reduction by

Fig. 8. (a) C₃H₆ oxidation profiles of the fresh Pd-LSM-SG (1), activated Pd-LSM-SG (2), fresh Pd-LSM-IM (3), activated Pd-LSM-IM catalysts (4), and fresh pure La_{0.7}Sr_{0.3}MnO₃ (5). (b) De-NO_x reaction at 200 °C over the fresh Pd-LSM-SG (1), activated Pd-LSM-SG (2), fresh Pd-LSM-IM (3), and activated Pd-LSM-IM (4) catalysts.

C₃H₆.

The amounts of exposed Pd and Pd dispersions of the fresh and activated catalysts were calculated using the CO chemisorption data in Fig. S11 by assuming a stoichiometric ratio of CO/Pd of 1:1, and the results are presented in Table 3. The amount of CO adsorbed on the perovskite support was measured and subtracted during the Pd dispersion calculations. The CO chemisorption results were in agreement with the XRD and XAFS results and indicated that the amount of exposed Pd species of the Pd-LSM-IM catalyst that was available for surface reactions was larger than that of the Pd-LSM-SG catalyst. The changes in Pd dispersion after the NSR reactions were negligible, which indicated that the Pd catalysts were stable during the NSR reaction and that the *in situ* activation behavior was caused by the changes in the oxidation state of Pd, rather than the amounts of Pd species.

For the TOF calculation, C₃H₆ was assumed to be activated only at the Pd sites, rather than at the Pd and Mn sites, because LSM was catalytically inert at 200 °C (Fig. 5(a)). The calculated TOF values are summarized in Table 3. For the fresh Pd-LSM-SG, fresh Pd-LSM-IM, and activated Pd-LSM-IM catalysts, the NO_x reduction reaction only occurred at the Pd²⁺ sites and the calculated TOFs for these catalysts were similar ($\sim 1.3 \times 10^{-3} \text{ s}^{-1}$). The reduction of NO_x over the activated Pd-LSM-SG catalyst occurred at both the Pd⁰ and Pd²⁺ sites. Therefore, the TOF of the activated Pd-LSM-SG catalyst was much higher ($5.3 \times 10^{-3} \text{ s}^{-1}$) than those of the aforementioned catalysts. To obtain the TOFs of the Pd⁰ and Pd²⁺ sites, we used the Pd 3d XPS profiles of the activated catalysts (Fig. S12) and corresponding surface Pd²⁺/Pd⁰ ratios (Table 2). The TOF of Pd⁰ for the acti-

vated Pd-LSM-SG catalyst was $10.6 \times 10^{-3} \text{ s}^{-1}$, which was eight-fold higher than that of Pd²⁺ ($1.3 \times 10^{-3} \text{ s}^{-1}$). Using both experimental data and kinetic calculations, we concluded that Pd⁰ was more active for the De-NO_x reaction than Pd²⁺.

3.5. Effects of H₂O and CO₂

Fig. 9 presents the De-NO_x activities of the catalysts in the presence of 5% H₂O and/or 5% CO₂. The conventional Pt/BaO/Al₂O₃ and Pd/BaO/Al₂O₃ catalysts were used as references. Both H₂O and CO₂ presented negative effects on the NO_x storage capacity (NSC) of the catalysts via competitive adsorption or the formation of hydroxide species [49,50]. Our results demonstrated that compared with H₂O, CO₂ had a more negative effect on the De-NO_x activity of both perovskite-based and conventional catalysts. The NRP of the Pd-free LSM catalyst decreased to 28.8% in the presence of H₂O and CO₂ (Fig. 9). The NRPs of the Pt/BaO/Al₂O₃ and Pd/BaO/Al₂O₃ catalysts were approximately 90%, and were similar to that of the activated Pd-LSM-SG catalyst in the absence of H₂O and CO₂. However, after exposure to H₂O and CO₂, the NRPs of the Pt/BaO/Al₂O₃ and Pd/BaO/Al₂O₃ catalysts decreased by 12.3% and 15.9%, respectively, and that of the Pd-LSM-SG catalyst decreased by only 5.8% to 84.3%. Furthermore, the Pd-LSM-IM catalyst presented higher tolerance to H₂O and CO₂ than the conventional catalysts, and its NRP decreased by 9.0% when exposed to H₂O and CO₂.

To elucidate the remarkable tolerance to H₂O and CO₂ of the Pd-LSM-SG catalyst, we used the NO oxidation results of the catalysts (Fig. S13). In the absence of H₂O and CO₂, the perov-

Table 3

Surface Pd contents and kinetic results at 200 °C.

Catalyst	<i>R</i> (mol g ⁻¹ s ⁻¹ × 10 ⁻⁸)	Exposed Pd atoms ^a (mol g ⁻¹ s ⁻¹ × 10 ⁻⁵)	Pd dispersion (%)	Pd TOF (s ⁻¹ × 10 ⁻³)	Pd ²⁺ TOF ^b (s ⁻¹ × 10 ⁻³)	Pd ⁰ TOF ^b (s ⁻¹ × 10 ⁻³)
Fresh Pd-LSM-SG	3.0	2.3	12.1	1.3	1.3	—
Activated Pd-LSM-SG	12.6	2.3	11.9	5.3	1.3	10.6
Fresh Pd-LSM-IM	6.4	5.9	30.1	1.1	1.1	—
Activated Pd-LSM-IM	7.3	5.8	29.4	1.3	1.3	—

^a Calculated using the CO temperature-programmed desorption data in Fig. S11.

^b Calculated using the Pd²⁺/Pd⁰ ratio obtained from the XPS results in Table 2.

Fig. 9. De-NO_x activity over the conventional and perovskite-based catalysts at 350 °C in the absence of H₂O and CO₂ (1) and in the presence of 5% H₂O (2), 5% CO₂ (3), and 5% H₂O and 5% CO₂ (4).

skite-based catalysts presented similar NO-to-NO₂ oxidation activity, which was higher than 60%. The conventional Pt/BaO/Al₂O₃ and Pd/BaO/Al₂O₃ catalysts presented lower NO-to-NO₂ conversions of 43.1% and 29.5%, respectively. These values decreased by 10%–15% in the presence of H₂O and CO₂. Compared with NO, NO₂ can be more efficiently and quickly trapped on basic sites [51,52]. Thus, a high NO₂/NO ratio would promote NO_x trapping under lean-burn atmospheres. This rationalized why the perovskite catalysts exhibited higher resistance to H₂O and CO₂ than the conventional Pt/BaO/Al₂O₃ and Pd/BaO/Al₂O₃ catalysts (Fig. 9). In addition, we compared the NSCs of the fresh and activated catalysts (Fig. S14) and concluded that, for the Pd-LSM-SG catalyst, the formation of Pd⁰ enhanced the regeneration ability of the NO_x storage sites in the presence of H₂O and CO₂. Approximately 90% of the stored NO_x species was released and reduced during the 10 s fuel-rich period, as illustrated in Fig. S14, which, in turn, enabled the Pd-LSM-SG catalyst to efficiently trap NO_x during the subsequent lean-burn period.

Fig. 10 depicts the De-NO_x activities of the perovskite-based catalysts at different O₂ concentrations in the absence and presence of H₂O and CO₂. Fig. S15 presents the corresponding NO_x concentration curves of the perovskite-based catalysts during the NSR tests. The De-NO_x activity of the activated Pd-LSM-SG catalyst monotonously increased as the O₂ concentration decreased from 8% to 2% in the absence of H₂O and CO₂ (Fig. 10). As illustrated in Fig. S15(a), the Pd-LSM-SG catalyst exhibited the highest NO_x reducing efficiency at the lowest O₂ concentration (2%), which could indicate that the amount of Pd⁰ species on the activated Pd-LSM-SG catalyst could be further increased by decreasing the O₂ concentration.

In the absence of H₂O and CO₂, the NSC of the activated Pd-LSM-SG catalyst was sufficient to completely trap NO_x during each lean-burn step even at an O₂ concentration of 2% (Fig. S15(a)). The De-NO_x activity was mainly determined by the NO_x reducing efficiency of the desorbed NO_x. However, the addition of H₂O and CO₂ led to the decrease in the NSC of the activated Pd-LSM-SG catalyst. The decrease in O₂ concentration en-

Fig. 10. De-NO_x activity of the sol-gel-prepared La_{0.7}Sr_{0.3}MnO₃-supported Pd (black lines) and wet-impregnation-prepared La_{0.7}Sr_{0.3}MnO₃-supported Pd (red lines) in the absence (solid lines) and presence (dashed lines) of H₂O and CO₂ as function of the O₂ concentration at 350 °C.

hanced this negative effect by decreasing the degree of NO oxidation, which led to a large NO_x slip during the lean-burn phases and therefore, lower De-NO_x activity, as illustrated in Fig. S15(b). Apparently, the oxidation of NO was of critical importance for the NO_x trapping and De-NO_x performance of the catalysts in the presence of H₂O and CO₂. Thus, high O₂ concentrations could improve the H₂O and CO₂ resistance of the perovskite-based catalysts.

The S tolerance of the perovskite-based catalysts was also investigated. Fig. 11 presents the De-NO_x activity of the perovskite-based catalysts after they were co-fed 125 ppm SO₂ for 1 h. The perovskite-based catalysts were highly resistant to S poisoning in both the absence and presence of H₂O and CO₂, whereas the conventional catalysts underwent significant deactivation (Fig. 11). For example, in the presence of H₂O, CO₂, and SO₂, the Pd-LSM-SG catalyst still achieved a promising De-NO_x activity of 76.2%. In contrast, the De-NO_x activities of the Pd/BaO/Al₂O₃ and Pt/BaO/Al₂O₃ catalysts decreased to 54.3% and 48.2%, respectively. The excellent S tolerance of the

Fig. 11. De-NO_x activities of the conventional Pd/BaO/Al₂O₃ (Pd/Ba/Al) and Pt/BaO/Al₂O₃ (Pt/Ba/Al) and perovskite-based catalysts at 350 °C in the absence of H₂O, CO₂ and SO₂ (1), in the presence of 125 ppm SO₂ (2), and 5% H₂O, 5% CO₂ and 125 ppm SO₂ (3).

Fig. 12. Product selectivity of the fresh Pd-LSM-SG (a) and activated Pd-LSM-SG (b) catalysts at 350 °C: N₂ (■), N₂O (▼), NO (▲), NO₂ (◆), and C₃H₆ (●). Feeding gas: 1000 ppm C₃H₆, 5 vol% H₂O, 5 vol% CO₂ balanced with N₂; space velocity: 120000 mL g⁻¹ h⁻¹.

perovskite-based catalysts could be explained by the relatively weak basicity of the NO_x storage sites on the perovskite support, which suppressed S trapping.

3.6. Selectivity of products

Fig. 12 presents the product selectivities of the perovskite-based catalysts in the presence of H₂O and CO₂. The fresh and activated Pd-LSM-SG catalysts were saturated with NO_x before the tests. After switching to the fuel-rich atmosphere, C₃H₆ reacted with the nitrates/nitrites in the catalysts and N₂, N₂O, NO, and NO₂ were released. For the fresh Pd-LSM-SG catalyst, a large amount of NO_x, mostly NO, slipped from the catalyst at the beginning of the NO_x reduction reaction, and a large amount of N₂O and low amount of N₂ were released (Fig. 12(a)). As previously reported [53], N₂O was a partially reduced product and was always produced at the onset of the regeneration phase, because the amount of instantaneously activated C₃H₆ was insufficient to reduce the entire amount of fast desorbed NO_x to N₂. As the NO_x reduction process proceeded, Pd⁰ species were gradually formed, which was beneficial for the activation of C₃H₆. Consequently, the C₃H₆ signals decreased to zero within 40 s after switching to the fuel-rich atmosphere, which indicated that at that point the entire amount of C₃H₆ was activated and was consumed for the NO_x reduction reaction. Accordingly, the N₂ production was promoted and reached a maximum after 110 s. After 150 s, the majority of the occupied NO_x storage sites was regenerated, and thus, small amounts of N₂ and other NO_x species were produced.

The activated Pd-LSM-SG catalyst presented excellent NO_x reduction performance owing to the presence of Pd⁰ species in its structure (Fig. 12(b)). The C₃H₆ in the fuel-rich atmosphere was rapidly activated on the Pd⁰ sites and reacted with the stored NO_x species, as indicated by the disappearance of the C₃H₆ signals within 10 s after the switch. Because of the higher C₃H₆ activation/utilization efficiency during the initial stage of the reaction, the amounts of NO_x slip and N₂O formed over the activated Pd-LSM-SG catalysts were much lower than those

formed over the fresh catalyst. In particular, N₂ became the only dominant product during the entire NO_x reduction process. The differences in product selectivity over the fresh and activated Pd-LSM-SG catalysts illustrated the determining role of Pd⁰ for the activation of C₃H₆ during the NO_x reduction reaction. Moreover, the differences in product selectivity indicated that N₂O mainly formed at the PdO sites, and the Pd⁰ sites favored the production of N₂ and inhibited the NO_x slip under fuel-rich atmospheres. This explained the differences in N₂ selectivity over the Pd-LSM-SG and Pd-LSM-IM catalysts during the NSR process.

4. Conclusions

In this study, we designed two well-defined catalysts with different Pd-perovskite interaction levels to identify the active Pd species for the NO_x reduction reaction. The Pd-LSM-SG catalyst presented an atypical *in situ* activation behavior during the NSR process, which boosted its De-NO_x activity to 90.1% and suppressed the production of N₂O and NO_x slip. This catalyst also presented outstanding tolerance to H₂O, CO₂, and SO₂, and achieved an excellent NRP of 76.2% in their presence. XAFS and XPS data revealed that the remarkable performance of the Pd-LSM-SG catalyst was ascribed to the *in situ* transformation of PdO to metallic Pd. The formed metallic Pd exhibited excellent C₃H₆ activation ability, and its TOF for the NO_x reduction reaction was eight-fold higher than that of PdO. However, the formation of Pd⁰ species was highly dependent on the strength of the Pd-perovskite interactions. Therefore, a trade-off existed between the Pd dispersion and amount of highly active Pd⁰. Although the excessive Pd-perovskite interactions were beneficial for increasing the dispersion of the Pd species, they hindered the formation of Pd⁰, and thus, lowered the De-NO_x performance of the Pd-LSM-SG catalyst. The MSI was used in this study as a key parameter and powerful tool for acquiring and identifying the active metal species under dynamic alternating oxidizing/reducing atmospheric conditions. This idea could be applied for designing other efficient catalysts that could be used under complex reaction atmospheres.

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Graphical Abstract

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Promoting NO_x reduction via *in situ* activation of perovskite supported Pd catalysts under alternating lean-burn/fuel-rich operating atmospheres

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A perovskite-supported Pd catalyst was *in situ* activated to generate Pd⁰ species under dynamic alternating oxidizing/reducing atmospheric conditions via tuning the metal-support interactions. The De-NO_x activity of the generated Pd⁰ species was eight fold higher than that of the Pd²⁺ species.

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贫燃/富燃循环气氛下原位活化Pd负载钙钛矿催化剂促进NO_x还原消除

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摘要: 稀燃发动机通过提高空燃比来改善燃油经济性, 减少CO₂排放。但由于空燃比较高, 稀燃发动机尾气中的NO_x无法通过传统的三效催化技术有效消除。为了解决这一问题, 适用于稀燃条件的NO_x储存还原(NSR)技术得到了开发和应用。传统的NSR催化剂以贵金属Pt作为其氧化还原活性中心。Pt基催化剂具有较高的NO_x消除活性, 然而热稳定性差, 高温下易团聚失活。据报道, Pd具有比Pt更好的热稳定性和抗硫性, 且能够在更低的温度下活化还原剂, 促进NO_x还原。但De-NO_x反应中的活性Pd物种至今尚无定论, 这对设计高效的Pd基NSR催化剂提出了挑战。

本文设计制备了具有高活性的Pd负载型钙钛矿催化剂(Pd-La_{0.7}Sr_{0.3}MnO₃)。其中钙钛矿组分的加入提高了Pd基催化剂的NO氧化能力和热稳定性, 并提供了可用于NO_x储存的碱性位点。通过调节金属-载体相互作用, 使Pd催化剂在NSR反应气氛下发生了自活化现象, 活化后催化剂的NO_x消除活性由56.1%提高到90.1%, 同时副产物N₂O的选择性降低。XRD、XAFS和XPS等表征结果显示, 在反应气氛下催化剂中的Pd²⁺被部分还原为高活性的Pd⁰物种。相较于Pd²⁺, Pd⁰表现出更强的活化C₃H₆的性能, 从而提高了催化剂在富燃阶段的NO_x还原效率。结合XPS、CO化学吸附和动力学的实验结果, 计算得出Pd⁰位点的NO_x还原速率是Pd²⁺位点的8倍, 从实验现象和动力学计算两个角度分别证明Pd⁰物种具有更优异的NO_x还原活性。

然而, Pd⁰物种的生成需要适当强度的金属-载体相互作用。通过与传统的Pd/BaO/Al₂O₃催化剂进行对比研究, 发现金属-载体相互作用过强时, 在富燃阶段Pd²⁺物种难以被还原, 且还原得到的Pd⁰物种并不稳定, 会在随后的贫燃阶段被快速重新氧化为Pd²⁺。强相互作用虽然可以降低Pd物种粒径, 提高Pd的分散度, 但由于无法产生高活性的Pd⁰物种, 催化剂的NO_x消除性能显著降低。此外, 相较于传统的Pd/BaO/Al₂O₃和Pt/BaO/Al₂O₃催化剂, Pd负载型钙钛矿催化剂具有更为优异的NO氧化能力, 且储存位碱性适中, 因而表现出更强的抗H₂O、CO₂和SO₂的性能, 具有良好的应用前景。本文的结果说明了金属-载体相互作用对催化剂活性的显著影响, 同时也为理解和设计应用于动态氧化/还原气氛的金属催化剂提供了新的思路。

关键词: 贫燃; 氮氧化物还原; 金属-载体相互作用; 原位活化; 钯

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