A review of NO\textsubscript{x} storage/reduction catalysts: mechanism, materials and degradation studies

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The catalytic removal of nitrogen oxides (NO\textsubscript{x}) from lean-burn exhaust emissions is one of the major challenges in environmental catalysis. Among the NO\textsubscript{x} emission control technologies, NO\textsubscript{x} storage/reduction (NSR) is currently regarded as one of the most practical technologies for lean-burn gasoline and diesel vehicles. This review gives a comprehensive overview of NSR technology, including the NSR reaction mechanisms, degradation mechanisms and NSR catalyst developments. The NSR reaction and degradation mechanisms will be addressed based on a typical NSR catalyst such as Pt/BaO/Al\textsubscript{2}O\textsubscript{3}, along with the concurrent new NSR catalyst developments for enhancing the NSR performance and alleviating their sulfur poisoning and thermal degradation.

1. Introduction

Conventional gasoline engines operate near stoichiometric conditions with an air to fuel ratio of 14.7 (for petrol).\textsuperscript{1,2} Lean-burn gasoline and diesel engines operate under lean-burn conditions with an air to fuel ratio higher than the stoichiometric combustion ratio (usually in the range of 20 : 1 to 65 : 1).\textsuperscript{3-5} Lean-burn engines are attracting more and more attention than conventional gasoline engines due to their higher fuel efficiency and lower CO\textsubscript{2} emission.\textsuperscript{3-8} However, under lean-burn conditions, the nitrogen oxides (NO\textsubscript{x}) exhaust emissions cannot be efficiently reduced over the classical three-way catalysts in the presence of excessive O\textsubscript{2}.\textsuperscript{3,6,9}

The NO\textsubscript{x} emissions have multi-fold hazards for the atmosphere, environment and human health, due to the formation of fine particles, ozone smog, acid rain and eutrophication.\textsuperscript{10} In the US, the NO\textsubscript{x} emissions from mobile vehicles contribute almost half of all NO\textsubscript{x} produced, and therefore, rigorous regulations were introduced for reducing NO\textsubscript{x} emissions from mobile vehicles.\textsuperscript{11}

To meet the more and more stringent NO\textsubscript{x} emission regulations, three technologies, including direct decomposition of NO\textsubscript{x}, selective catalytic reduction (SCR) of NO\textsubscript{x} and NO\textsubscript{x} storage/reduction (NSR), have been developed for the control of lean-NO\textsubscript{x} emissions.\textsuperscript{9,12} The direct decomposition of NO\textsubscript{x} is thermodynamically favorable at temperatures below 900 °C, but the activation energy is relatively too high.\textsuperscript{13} Cu-ZSM-5 has been extensively studied as the most promising catalyst for direct NO\textsubscript{x} decomposition in 1990s.\textsuperscript{14} However, its poor activity with ~10% of NO\textsubscript{x} decomposed together with a low thermal stability has hindered its use in practice.\textsuperscript{15,16} SCR technologies have been extended to urea/ammonia-SCR,\textsuperscript{17} hydrocarbon-SCR,\textsuperscript{18} and plasma-assisted SCR.\textsuperscript{19} Among them, urea/ammonia-SCR is a widely commercialized technology for NO\textsubscript{x} removal in stationary sources and heavy-duty vehicles. However, the adoption of urea/ammonia-SCR technology to lean-burn engines results in complex exhaust after treatment system and enforcement difficulties. The NSR technology was first developed by Toyota researchers in 1995,\textsuperscript{20-22} which does not require an additional reducing agent. The NO\textsubscript{x} emissions are first trapped in the storage materials of NSR catalysts under lean conditions and then reduced by reducing agents under rich conditions. Although NSR technology is regarded as the most practical technology for lean-burn gasoline and diesel vehicles, the role of every component in the NSR performance and the inter-component relationship are still not very clear.\textsuperscript{9,23} Meanwhile, the state-of-the-art NSR catalyst (Pt/BaO/Al\textsubscript{2}O\textsubscript{3}) is weakly resistant to sulfur poisoning and thermal treatment.\textsuperscript{9}

In this work, we review the NSR reaction mechanism and address the role of each component in a typical NSR catalyst (Pt/BaO/Al\textsubscript{2}O\textsubscript{3}) during the whole reaction process. Meanwhile, NSR degradation mechanisms, especially on sulfur poisoning and thermal degradation, are addressed. Concerning the existing problems of typical NSR catalysts, the latest developments of new NSR catalysts are also reviewed. Finally, major conclusions and some research directions are presented.

2. Mechanism of NSR reactions

NSR catalysts are generally comprised of precious metals, NO\textsubscript{x} storage components and support metal oxides, with
Pt/BaO/Al₂O₃ as the most typical NSR catalyst. NSR catalysts work under cyclic operations with periodic switches between lean and rich conditions. When an engine runs in the lean-burn cycle, NOₓ is trapped in the storage component of the NSR catalyst. Upon engine runs in the rich-burn cycle, the released NOₓ from storage components is reduced to N₂ on precious metal. Usually a lean-burn cycle lasts 1–2 minutes followed by a 3–5 second rich-burn operation. Researchers also explored the NSR catalyst performance with long rich regeneration periods (for example, 1500 seconds). Under such conditions, the outlet NOₓ concentration during cyclic operation decreased, however, with higher fuel consumption.

The NSR reaction mechanism during lean and rich cycles can be assumed to contain the following five steps: 9,23
(I) NO oxidation to NO₂;
(II) NOₓ (NO and NO₂) sorption on the surface of alkali and/or alkaline-earth adsorption sites in the form of nitrites or nitrates;
(III) reducing agents (such as H₂, CO, hydrocarbons) evolution from the rich exhaust gas;
(IV) NOₓ release from the nitrite or nitrate sites;
(V) NOₓ reduction to N₂.

Steps I and II occur during lean-burn cycles and Steps III, IV and V happen during rich-burn cycles. Fig. 2 schematically illustrates the possible mechanism of NOₓ storage/reduction in a typical Pt/BaO/Al₂O₃ catalyst. First, under lean-burn conditions, NO is oxidized to NO₂ on the precious metal Pt. After that, the NO and NO₂ are adsorbed on the surface of BaO by the formation of barium nitrites or nitrates. Under rich-burn conditions, the released NOₓ from barium nitrites or nitrates are reduced to N₂ on the Pt surface by H₂, CO, and/or hydrocarbons from the rich exhaust gas.

In this section, we discussed the five-step NSR mechanism. Despite a general agreement on the NSR mechanism currently, the understanding of each step in the NSR mechanism is still not very clear, especially the last three steps regarding the NSR catalysts regeneration. More systematic and detailed experimental and modeling research is expected to help better understand the NSR mechanism in order to achieve more efficient NSR catalysts.

3. Roles of each component in the Pt/BaO/Al₂O₃ catalyst during NSR reactions

As discussed in Section 2, there are five steps in a cycle of NOₓ storage/reduction reactions. Each step is critical for efficient operation, with each component of the Pt/BaO/Al₂O₃ catalyst holding important functions during the NSR reactions. In the following section, the roles of each catalyst component in different NSR reaction steps will be discussed individually. The effect of gas composition will be discussed on the functions of each component in different NSR reaction steps as well.

3.1 Roles of Pt

Pt plays several key roles in the NOₓ storage/reduction reaction steps, such as (I) NO oxidation under lean-burn conditions, (II) NOₓ storage under lean-burn conditions, and (III) NOₓ reduction under rich-burn conditions. Although different NOₓ trapping components and support metal oxides will affect the functions of Pt in the NSR reactions, in this section, we will focus on the functions of Pt on BaO/Al₂O₃ in the NSR reactions.

3.1.1 NO oxidation step. In the lean-burn exhaust, with most of the NOₓ being NO, NO oxidation to NO₂ is a significant step in the overall NSR mechanism, since the NSR trapping component (BaO) is more effective in adsorbing NO₂ compared to NO. The NO oxidation primarily takes place on Pt. The NO oxidation on Pt can be either kinetically or thermodynamically controlled in the real lean-burn engine operation conditions. Fig. 3 shows the steady-state and equilibrium NO–NO₂ conversion in the temperature range of ~90–500 °C on the Pt/BaO/Al₂O₃ catalyst. It is shown that the steady-state NO conversion reaches a maximum of 60% at
Above 350 °C, NO conversion is limited by thermodynamic NO/NO₂ equilibrium, whereas, below 350 °C NO conversion is limited by kinetics and mass transfer. Considering the reversible adsorption and desorption of NO, O₂, and NO₂, Bhatia et al. referred to the microkinetic modeling studies of NO oxidation by Xu et al. and assumed that the NO oxidation happened by the following steps:

Step 1: NO + Pt → NO–Pt
Step 2: O₂ + 2Pt → 2O–Pt
Step 3: NO–Pt + O–Pt → NO₂–Pt + Pt
Step 4: NO₂–Pt → NO₂ + Pt

Interestingly, Xu et al. suggested that the O₂ adsorption/dissociation on Pt (Step 2) was the rate-determining step, while the density functional theory (DFT) calculation on NO oxidation to NO₂ by Smeltz et al. suggested the dissociation of atomic O from the O–Pt was the rate determining step (Step 3). However, Mulla et al. and Bhatia et al. were convinced that O₂ adsorption was the rate-determining step based on the microkinetic analysis using the global model. The actual NO oxidation mechanism still remains unclear and a detailed elementary kinetic model should be developed to explain the NO oxidation reactions.

Pt in Steps 1 to 4 refers to a vacant Pt site and oxides formation (PtO and PtO₂), which has been certified to decrease the activity of Pt for the NO oxidation. Fig. 4 shows the NO conversion results on Pt/Al₂O₃ with various pretreatments. Here, the absence of NO₂ trapping component (BaO) would decrease the storage of NO₂. The NO conversion was the highest when the catalyst was pretreated with reductive gas, whereas the lowest with NO₂ pretreatment. Olsson and Fridell also investigated the poisoning effect of NO₂ and O₂ on the NO oxidation on Pt/Al₂O₃ and Pt/BaO/Al₂O₃ catalysts. From the XPS analysis of the Pt/Al₂O₃ and Pt/BaO/Al₂O₃ catalysts after different pretreatments (Fig. 5 and Table 1), the Pt was further oxidized to Pt oxides by NO₂ other than O₂. Due to the highly oxidizing nature of NO₂, NO₂ can be an effective source of atomic oxygen. The chemisorbed oxygen on Pt prevents the adsorption of NO, thus inhibiting the NO oxidation. The presence of BaO enhances the formation and stability of less reactive Pt oxides. Meanwhile, BaO also reduces the Pt exposed surface area by its physical blockage of Pt sites or formed nitrate species. These two reasons result in the lower NO oxidation on Pt/BaO/Al₂O₃ than that on Pt/Al₂O₃.

The effect of Pt dispersion on the NO oxidation has been widely investigated. The strong impact of the Pt particle size on the NO oxidation rate suggests that NO oxidation is a structure sensitive reaction. As the Pt dispersion decreases, the Pt activity for NO oxidation increases. The reason for this may be that the larger Pt particles form less surface Pt oxides, thus are less active for NO oxidation.

### 3.1.2 NOₓ storage step

Pt does not play a role in NOₓ trapping directly. However, the amount of NO₂ (as a result of catalytic NO oxidation on Pt) on the catalyst surface significantly affects the NOₓ sorption, since NO₂ is more
effectively trapped by BaO.40–44 Meanwhile, Pt also plays a significant role in forming stable nitrate species by supplying atomic oxygen to the nearby nitrite species.45

Büchel et al.46 applied a two-nozzle flame spray pyrolysis method to prepare two NSR catalysts with Pt on either Al- or Ba-components without altering the Al2O3 or BaCO3 crystal sizes, Al/Ba weight ratio and Pt dispersion. Fig. 6 shows a set of transmission electron microscopy (TEM) images of Pt–Al–Ba (Pt preferentially deposited on Al2O3) and Al–Ba–Pt (Pt preferentially deposited on BaCO3) and the corresponding energy-dispersive X-ray (EDX) spectra of the two catalysts. The influence of Pt location on BaCO3 or Al2O3 has been studied during \( \text{NO}_x \) storage/reduction. They found that Pt on Al2O3 exhibited a better NO oxidation activity which was the limiting step for the overall \( \text{NO}_x \) storage process at low temperature (<300 °C). So, the Pt–Al–Ba catalyst performs better for \( \text{NO}_x \) storage than the Al–Ba–Pt catalyst at <300 °C. However, at high temperature (>350 °C), the location of Pt barely affected the \( \text{NO}_x \) storage performance.

### 3.1.3 \( \text{NO}_x \) reduction step

The \( \text{NO}_x \) reduction is the final step in the overall NSR reactions. In this step, the \( \text{NO}_x \) reduction happens on the Pt surface. The type of reductants, amount of reductants and operating temperatures all affect the Pt performance on the \( \text{NO}_x \) reduction.9,47

When using hydrocarbons as reductants, two general mechanisms have been reported for the \( \text{NO}_x \) reduction on NSR catalysts. One mechanism is based on the NO decomposition on Pt sites,48–50 and the other is based on the direct reaction between \( \text{NO}_2 \) and reductants.51,52 Previous studies indicated that different types of hydrocarbon lead to different \( \text{NO}_x \) reduction mechanisms.53,54 Due to the appearance of different reductants in the rich-burn cycle, it is difficult to distinguish between the two mechanisms. As summarized by Burch,55 the subtle changes in operating conditions would also affect the \( \text{NO}_x \) reduction mechanism. Therefore, multiple \( \text{NO}_x \) reduction mechanisms may exist during the \( \text{NO}_x \) reduction on NSR catalysts.

No matter through which mechanism \( \text{NO}_x \) is reduced, the research results indicate that \( \text{NO}_x \) reduction occurs on the

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<th>Catalyst</th>
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<td>20</td>
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**Table 1** Relative abundance of different Pt species from fitting of XPS data taken after pretreatment in NO2 or O2 (Fig. 5). Reproduced from ref. 30 with permission from Elsevier.
precious metal (Pt for the Pt/BaO/Al2O3 catalyst). In addition, the similar Pt particle size effect for NO oxidation was found for NO2 reduction.56 Large Pt particles were found to be more efficient for NO2 reduction than small ones since larger Pt particles tend to suppress the formation of Pt oxides and expose the Pt metal as the NO2 reduction catalyst.

Apart from hydrocarbons as reductants for the NO2 reduction, other reductants, such as H2 and CO, are also investigated for achieving high NO2 reduction.57,58 H2 is more efficient for NO2 reduction than CO, especially at low temperatures (<150 °C), due to the CO’s poisoning effect on Pt sites as a result of the strong adsorption of CO on Pt sites. However, at high temperatures (>350 °C), CO and hydrocarbons have similar activities as H2 for NO2 reduction.

3.2 Roles of BaO

BaO is the most commonly studied NOx trapping component among metal oxides,59–62 with a major contribution to the overall NOx trapping capacity. Besides the NOx storage step, BaO also plays some roles in the NO oxidation, NOx release and NOx reduction steps. Although different metal oxide supports and precious metal components affect the functions of BaO in the NSR reactions, in this section, we still focus on the general functions of BaO of the Pt/BaO/Al2O3 catalyst in the NSR reactions.

3.2.1 NOx oxidation step. As reviewed in Section 3.1.1, BaO presents some negative effects on the NO oxidation, as a result of its blockage of the Pt surface and stabilization effect on the Pt oxides (inactive for the NO oxidation).

3.2.2 NOx storage step. As the most typical NOx trapping component, BaO’s NOx trapping capacity is affected by gas composition, temperature and the Pt–BaO proximity.9 According to the literature, different NOx trapping mechanisms have been proposed.44,63–66 However, due to the complexity of the NOx trapping reactions, it is difficult to identify and differentiate which of the mechanisms exactly happened during the NOx trapping process. Both nitrates and nitrates are detected on the NSR catalyst after NOx trapping. So it is well accepted that there must be a nitrite route and a nitrate route for the NOx trapping on the Pt/BaO-Al2O3 catalyst.65,66

In the nitrite route, it is proposed that NO is oxidized on Pt sites and directly trapped by nearby BaO sites to form Ba-nitrates. The Ba-nitrates are finally oxidized to Ba-nitrates. In the nitrate route, it is proposed that NO is oxidized to NO2 on Pt sites. NO2 spills over to the BaO site to form Ba-nitrate with evolution of NO. Fig. 7 shows the two different mechanisms for NO oxidation and the followed NOx oxidation on the Pt/BaO/Al2O3 catalyst. The Ba loading affects which route is dominating during the NOx trapping step.67 When Ba loading is high or low, there are more or less Ba sites that are close to the Pt sites, which lead to the predominance of the nitrite route or nitrate route.

According to the literature, BaO is more effective to trap NO2 than to trap NO. Therefore, the effect of NOx composition and temperature on the BaO trapping capacity is actually related to its effect on the NOx oxidation.68 At high temperature, no matter whether NO or NO2 is used as the NOx precursor, similar NOx trapping capacity is observed on the Pt/BaO/Al2O3 catalyst. This is because NO can be easily oxidized to NO2 at high temperature. However, at low temperature, the NOx trapping capacity of BaO is low when using NO as a NOx precursor due to the limited NO oxidation into NO2.

With the NOx trapping BaO, the H2O and CO2 in the exhaust could react to produce barium hydroxide and carbonate. Lietti et al.69,70 found that BaO, Ba(OH)2 and BaCO3 coexist at the catalyst surface at 360 °C and the NOx trapping occurs at the BaO sites first, then the Ba(OH)2 and finally the BaCO3. The NOx trapping order on different Ba-based components is derived from the sequence of the evolved H2O and CO2, as shown in Fig. 8. The H2O and CO2 evolutions are due to the decompositions of Ba(OH)2 and BaCO3, respectively. As shown in Fig. 8a, in the first cycle, NOx slip was detected after about 50 s and CO2 evolution was observed at the same time with NOx slip. This reveals that the BaO reacts with NOx in the first 50 s, with no placed product evolution. Then, BaCO3 is decomposed to form the Ba(NO3)2. In the first cycle, there is barely H2O evolution during the whole testing time. This is because the tested Pt/BaO/Al2O3 catalyst was pretreated in dry air. So there is no surface hydroxyl species and Ba(OH)2 on the catalyst surface. As shown in Fig. 8b, in the second cycle, NOx slip was detected after about 250 s and CO2 evolution was again observed coincident with NOx slip. This reveals that the BaO reacts with NOx in the first 50 s, with no placed product evolution. Then, BaCO3 is decomposed to form the Ba(NO3)2. So there is H2O evolution in the second cycle. From the results shown in Fig. 8b, it is obvious that Ba-based components decomposed in the order of Ba(OH)2 < BaCO3. Since there is no new BaCO3 produced during the testing (no CO2 in the regeneration process) and much of the BaCO3 has been decomposed during the first two cycles, the CO2 evolution is very small in the third cycle.

The thermodynamic stability of BaCO3 is higher than Ba(OH)2. Different from BaO, in order to trap NOx, Ba(OH)2 and BaCO3 must decompose first and then react with NOx. Therefore, the presence of H2O and CO2 in the exhaust gas phase will affect the rate of NOx trapping. Epling et al.71,72 studied the effect of CO2 and H2O on the NOx trapping capacity of NSR catalysts and they found that the presence of H2O and CO2 during the lean-burn phase decreases the NOx trapping capacity. In addition, CO2 decreases more NOx trapping capacity than H2O. Moreover, Hodjati et al.80,81...
Apart from the reductant gases and O$_2$, the presence of other gases, such as H$_2$O and CO$_2$, also affects the NO$_x$ release during the rich-burn cycle. The presence of H$_2$O reduces the NO$_x$ release, while CO$_2$ increases the NO$_x$ release.$^{9,75}$

### 3.3 Roles of Al$_2$O$_3$

Al$_2$O$_3$ is widely used as the support for NSR catalysts due to its high surface area and high thermal stability. The important role of Al$_2$O$_3$ in NSR catalysts is to help in dispersing noble metals and NO$_x$ trapping materials. Al$_2$O$_3$ can also adsorb a little amount of NO$_x$ by forming Al-nitrate species.$^{76}$ However, due to Al-nitrate’s low thermal stability and small amount, the NO$_x$ trapping by Al$_2$O$_3$ is usually neglected.

In the above Section 3, we reviewed the roles of each component of a typical NSR catalyst (Pt/BaO/Al$_2$O$_3$) in different NO$_x$ storage/reduction reaction steps. The gas composition effect on each component’s functions during different NSR reaction steps was also detailed. Clear understanding of the roles of each component of the Pt/BaO/Al$_2$O$_3$ catalyst in the NSR process is very important to further increase NSR efficiency of this type of NSR catalyst and, the development of more efficient NSR catalysts. However, there are still debates on how Pt/Ba proximity, Pt and Ba loadings, Pt particle morphology, and the Pt/BaO, Pt/Al$_2$O$_3$ and BaO/Al$_2$O$_3$ interactions affect the NO$_x$ storage/reduction activity. In addition, the lean-rich operating conditions have a strong influence on the catalytic activity of NSR catalyst. Further understanding of these questions will help to understand the Pt/BaO/Al$_2$O$_3$ catalyst and the NSR mechanism.

### 4. Deactivation mechanism of NSR catalysts

Sulfur poisoning, thermal degradation and carbon deposition are the primary deactivation mechanisms that affect the application of NSR catalysts. In the following section, we will discuss in detail how these three deactivation mechanisms influence the key components in the typical Pt/BaO/Al$_2$O$_3$ NSR catalyst and the NSR performance.

#### 4.1 Sulfur poisoning

In typical lean exhaust, sulfur is mainly present in the form of SO$_2$. During the lean-burn cycle, SO$_2$ can poison not only the basic NO$_x$ trapping component but also the metal oxide support. In addition, during the rich-burn cycle, sulfur can also accumulate on the precious metal component, and therefore decrease its NO$_x$ reduction and the following NO oxidation activities remarkably.

**4.1.1 Effect on Pt.** As reviewed in the previous sections, Pt plays important roles in the NO oxidation and NO$_x$ reduction. The poisoning of Pt active sites will decrease the NSR performance dramatically. When SO$_2$ was introduced during lean conditions, no poisoning of Pt by sulfur is typically observed. This is due to the rapid sorption of SO$_2$ by other catalyst components, especially the NO$_x$ trapping component BaO. However, when SO$_2$ was introduced during rich conditions, Pts species are detected on the catalyst surface, which reduce the NO$_x$ reduction activity of Pt.$^{77,78}$

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**Fig. 8** A sequence of the evolution of displaced H$_2$O and CO$_2$ during the NO$_x$ storage at 350 °C on a previously unused (fresh) Pt/BaO/Al$_2$O$_3$ catalyst. The data set in (b) was obtained in the cycle immediately following the data shown in (a). (c) was obtained immediately after the cycle depicted in (b). The lean phase contained 1000 ppm NO, 3% O$_2$, and a balance of He. The regeneration phase prior to each of the data sets contained 2000 ppm H$_2$ in a balance of He. Reproduced from ref. 69 with permission from Elsevier.

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3.2.3 NO$_x$ release step. The release of NO$_x$ is very important for efficient regeneration of NO$_x$ trapping sites and the following NO$_x$ reduction process. NO$_x$ release is induced by the decomposition of Ba-nitrites and Ba-nitrates upon high temperature and rich excursion (reductant introduction). The stability of Ba-nitrites and Ba-nitrates decreases with increasing temperature and decreasing O$_2$ partial pressure, causing their decomposition so as to release NO$_x$. 

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Surprisingly, Amberntisson et al.\textsuperscript{79,80} observed that the introduction of SO\textsubscript{2} at 400 °C enhanced the NO oxidation ability on Pt/BaO/Al\textsubscript{2}O\textsubscript{3} during the lean-burn cycle. This was attributed to the inhibition of the Pt oxides formation in the presence of SO\textsubscript{2}. As reviewed previously, Pt metal is considered the active sites for the NO oxidation. Less Pt oxides contribute to a higher NO oxidation ability.

Engstrom et al.\textsuperscript{81} found that the NO oxidation activity was remarkably decreased at the beginning of the lean-burn cycle when high concentration sulfur was introduced during the rich-burn cycle. This is because a large amount of PtS was produced during the rich conditions. Therefore, at the beginning of the lean-burn cycle, there were not enough Pt sites for the NO oxidation, since a large amount of PtS needs to decompose to release Pt sites. In addition, no matter whether the SO\textsubscript{2} was introduced during lean or rich conditions, the NO\textsubscript{x} reduction was dramatically inhibited by the presence of sulfur. The low NO\textsubscript{x} reduction was attributed to the blockage of Pt sites by PtS formed during the rich conditions.

4.1.2 Effect on BaO. The significant issue of the NSR catalyst with BaO as the NO\textsubscript{x} trapping component is sulfur resulting deactivation. NO\textsubscript{x} and SO\textsubscript{2}, both as acidic gases, are competitive for the Ba sites, and BaSO\textsubscript{4} is easier to form than Ba(NO\textsubscript{3})\textsubscript{2} due to its higher thermodynamic stability. The formation of BaSO\textsubscript{4} hinders the NO\textsubscript{x} sorption and therefore decreases the NO\textsubscript{x} trapping capacity of the Pt/BaO/Al\textsubscript{2}O\textsubscript{3} catalyst.\textsuperscript{82-85}

When SO\textsubscript{2} was introduced during the lean-burn cycle, BaSO\textsubscript{4} was observed. In addition, if the SO\textsubscript{2} dose is small, BaSO\textsubscript{4} is primarily observed on the surface\textsuperscript{86,87} and, if the SO\textsubscript{2} dose increases continuously, bulk BaSO\textsubscript{4} is also observed.\textsuperscript{78,87,88} Meanwhile, H\textsubscript{2}O\textsuperscript{89} and CO\textsubscript{2}\textsuperscript{90} evolution were detected when introducing SO\textsubscript{2} to the NSR catalyst. This reveals that SO\textsubscript{2} also displaces the common NO\textsubscript{x} trapping precursors, Ba(OH)\textsubscript{2} and BaCO\textsubscript{3}. Interestingly, when SO\textsubscript{2} was introduced during the rich-burn cycle, no sulfur sorption on Ba or a Ba–S interaction was observed.\textsuperscript{78}

Two mechanisms for SO\textsubscript{2} deactivation over the Pt/BaO/Al\textsubscript{2}O\textsubscript{3} catalyst have been proposed.\textsuperscript{91} Under lean conditions, SO\textsubscript{2} is oxidized on Pt sites to SO\textsubscript{3}, which is subsequently adsorbed by the Ba trapping components to form surface BaSO\textsubscript{4}. As the sulfation continues, the surface BaSO\textsubscript{4} migrates into the bulk phase. Under rich conditions, the deactivation is initially related to the Pt poisoning. As discussed in Section 4.1.1, PtS forms on the Pt sites, which blocks the Pt surface and hinders the NO\textsubscript{x} reduction and NO oxidation. However, ultimately the deactivation is still primarily due to the loss of NO\textsubscript{x} trapping sites by the formation of sulfates.

4.1.3 Effect on Al\textsubscript{2}O\textsubscript{3}. Al(SO\textsubscript{4})\textsubscript{2} has also been observed either in the presence of Pt or not. Although the formation rate of Al(SO\textsubscript{4})\textsubscript{2} is much lower than that of BaSO\textsubscript{4},\textsuperscript{91} the formation of Al(SO\textsubscript{4})\textsubscript{2} could further decrease the NSR catalyst performance since Al(SO\textsubscript{4})\textsubscript{2} would plug catalyst pores and limit the availability of active sites.\textsuperscript{92}

4.2 Desulfation

As discussed in the above sections, sulfur will poison the key components of the NSR catalyst, especially the Pt and BaO. Therefore, periodic sulfur removal from the NSR catalyst surface is required in order to recover the catalyst surface and keep an acceptable NSR performance.

The desulfation is usually carried out at high temperature (> 600 °C) under rich conditions. H\textsubscript{2} has been demonstrated to be more effective for desulfation than CO and other hydrocarbons.\textsuperscript{20,93,94} However, further research by Liu and Anderson\textsuperscript{95} revealed that in the absence of Pt, the addition of H\textsubscript{2} during the desulfation process actually hinders sulfur removal from the catalyst surface. They proposed that H\textsubscript{2} needs to be dissociated on Pt to reduce sulfate species subsequently.

The rich feed composition also influences desulfation efficiency. It has been reported that the presence of CO\textsubscript{2} and H\textsubscript{2}O\textsuperscript{97} has some positive effect on desulfation. During the desulfation process, BaSO\textsubscript{4} will transform to BaS, which is also very stable and difficult to be recovered. However, with addition of CO\textsubscript{2} into the rich feed, BaCO\textsubscript{3} will form and decrease the chance to form BaS. As studied by Mahzouli et al.,\textsuperscript{97} the presence of H\textsubscript{2}O in the rich feed can lower the desulfation temperature. The first proposed effect of H\textsubscript{2}O could be the same with CO\textsubscript{2}, in favor of the formation of less stable Ba(OH)\textsubscript{2} instead of BaS. The second proposed function of H\textsubscript{2}O is the easy transformation of PtS to PtO in the presence of H\textsubscript{2}O by the reaction: PtS + H\textsubscript{2}O → PtO + H\textsubscript{2}S.\textsuperscript{98}

Apart from operating conditions that influence the desulfation efficiency, NSR catalyst formulation also plays significant roles. As reported in the literature, Pt reduces the onset temperature for desulfation,\textsuperscript{20} while Rh in the NSR catalyst not only reduces the sulfur deactivation, but also increases the desulfation efficiency.\textsuperscript{99} As for NO\textsubscript{x} trapping components, the addition of Li, Na and/or K to BaO-based NSR catalysts will reduce the desulfation temperature.\textsuperscript{92} This is probably due to the formation of the less stable sulfates with the added alkali metals. The oxide support composition also affects the sulfur resistance and the desulfation process. For example, the Pt/BaO/CeO\textsubscript{2} shows better sulfur resistance than the Pt/BaO/Al\textsubscript{2}O\textsubscript{3} catalyst.\textsuperscript{99} Furthermore, the desulfation over Pt/BaO/CeO\textsubscript{2} proceeds at relatively mild conditions compared to those over Pt/BaO/Al\textsubscript{2}O\textsubscript{3}. This will be discussed in more detail in Section 5.

4.3 Thermal degradation

As discussed in the previous subsections, sulfate formation at the NO\textsubscript{x} trapping sites leads to a decrease of NO\textsubscript{x} trapping capacity, and hence degrades the NSR catalyst performance. Therefore, periodical sulfur removal from the NSR catalyst surface (desulfation) at high temperature (> 600 °C) is needed to recover NSR catalyst performance to an acceptable level. Thermal degradation of NSR catalysts is primarily caused by this high temperature desulfation treatment. In addition, during a rich-burn cycle, the oxidation of hydrocarbon, CO and H\textsubscript{2}, generates heat at the catalyst surface and results in thermal degradation as well.
4.3.1 Effect on Pt. Graham et al.\textsuperscript{100} investigated the effects of temperature and gas phase composition on the agglomeration of Pt particles in Pt/BaO/Al\textsubscript{2}O\textsubscript{3} catalysts. Not surprisingly, Pt particles agglomerated more severely as temperature increases from 600 to 950 °C with the Pt particle size increasing from 1–3 nm to 18 nm. In addition, Pt agglomeration at high temperature is also related to the gas phase composition. As shown in Fig. 9, as the O\textsubscript{2} concentration increased from 0.006% to 6.7%, the intensity of the Pt(311) peak increased from 16 to 82, with the Pt particle size increasing from 5 to 27 nm. Interestingly, the aging treatment at 950 °C in 1% H\textsubscript{2} atmosphere did not make remarkable Pt agglomeration compared with the fresh catalyst. Fig. 10 shows the TEM images and the corresponding particle size distribution histograms of fresh catalysts, aged catalysts at 950 °C in 1% H\textsubscript{2} and 6.7% O\textsubscript{2}. The histograms in Fig. 10 reveal the 1–3 nm Pt particles for the fresh catalyst, while ~2–6 nm for the Pt particles aged at 950 °C in 1% H\textsubscript{2}. However, the Pt particles aged at 950 °C in 6.7% O\textsubscript{2} show a bimodal distribution, ~1–5 nm and ~6–40 nm. The more severe Pt agglomeration may be due to vapor-phase transport of volatile Pt oxides, which accelerates the Pt agglomeration.\textsuperscript{101}

As discussed previously, the activity of NO oxidation and NO\textsubscript{x} reduction on Pt increases with the increasing Pt particle size. However, Li\textsuperscript{87} and Parks\textsuperscript{9} et al. reported that the activities of NO oxidation and NO\textsubscript{x} reduction on Pt decreased after a long-term thermal treatment at high temperature owing to a significant Pt surface area loss.

4.3.2 Effect on BaO. The formation of spinel BaAl\textsubscript{2}O\textsubscript{4} at high temperature has been reported as one of the thermal degradation mechanisms. Jang et al.\textsuperscript{102} reported that Ba in Pt–Ba/Al\textsubscript{2}O\textsubscript{3} reacted with Al\textsubscript{2}O\textsubscript{3} to form Ba–Al solid alloy above 550 °C and then transformed into stable BaAl\textsubscript{2}O\textsubscript{4} with a spinel structure. Fig. 11 shows the X-ray diffraction (XRD) patterns of Pt–Ba/Al\textsubscript{2}O\textsubscript{3} catalysts thermal treated for 24 h at temperatures from 550 to 1050 °C and pure BaAl\textsubscript{2}O\textsubscript{4} powder. As the aging temperature increased from 550 °C to 850 °C, a few new peaks at 19.6°, 28.3°, 34.3°, and 42°–43° appeared and their intensities increased gradually as the aging temperature increased further. These new peaks were assigned to BaAl\textsubscript{2}O\textsubscript{4} (222), (242), and (424) crystal planes.

X-Ray photoelectron spectroscopy (XPS)\textsuperscript{102} and Fourier transform infrared (FT-IR) spectra\textsuperscript{103} were also applied to confirm the reaction between Ba and Al\textsubscript{2}O\textsubscript{3} at high temperature. It was revealed that the Ba and Al could exist as isolated BaO dispersed on Al\textsubscript{2}O\textsubscript{3} in the fresh catalyst, but after aging above 800 °C, BaO and Al\textsubscript{2}O\textsubscript{3} interact with each other to form stable BaAl\textsubscript{2}O\textsubscript{4}.

Szailer et al.\textsuperscript{103} investigated the formation of BaAl\textsubscript{2}O\textsubscript{4} as a function of Ba loading on Al\textsubscript{2}O\textsubscript{3}. When the Ba loading was less than 8 wt%, there was no BaAl\textsubscript{2}O\textsubscript{4} observed, even with increasing aging temperature to 1000 °C. However, when the Ba loading increased to 20 wt%, the formation of BaAl\textsubscript{2}O\textsubscript{4} was observed at 800 °C. The formation of BaO is low, only a thin layer of BaO forms on the Al\textsubscript{2}O\textsubscript{3} surface. Therefore, without bulk BaO, no BaAl\textsubscript{2}O\textsubscript{4} forms.

Most of the researchers concluded that BaAl\textsubscript{2}O\textsubscript{4} decreases the NO\textsubscript{x} trapping capacity. As reported by Fekete et al. and

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Jang et al. 102,104 (Fig. 12), the NOx conversion efficiency of the Pt–Ba/Al2O3 catalyst decreased from 86 to 55% after aging at 750 °C for 24 h. On the other hand, BaAl2O4 was reported as a potential NOx trapping component. However, further detailed studies revealed that the nitrates formed on the BaAl2O4 surface cannot be easily regenerated without the presence of Pt. Meanwhile, the temperature window for NOx sorption on BaAl2O4 is very narrow, usually below 350 °C, since the nitrates formed on the BaAl2O4 surface are not stable above 350 °C. Therefore, according to the literature, the formation of BaAl2O4 decreases NOx trapping capacity for NSR catalysts during the real cyclic operation.

4.4 Carbon deposition

Carbon deposition on Pt sites by the decomposition of CO and hydrocarbons (C2H4, C3H6) is another deactivation mechanism that may lead to a progressive decay in NSR performance. Carbon can be deposited on Pt sites according to the following reactions: CO + Pt → Pt–CO and Pt–CO + Pt → Pt–C + Pt–O. 32 In addition, over Pt sites, C2H4 can be decomposed to carbon by these reactions: C2H4 + Pt → Pt–C2H4 and Pt–C2H4 + 4O → CO2 + H2O + Pt–C. 105 Although Pt–Ba/Al2O3 is a potential soot oxidation catalyst, the remained carbon on the Pt sites hinders the NO oxidation and NOx reduction.

In Section 4, we reviewed the degradation mechanisms of the Pt/BaO/Al2O3 catalyst, especially focusing on the sulfur poisoning and thermal degradation of the key components of the Pt/BaO/Al2O3 catalyst, and the influence of these degradations on the NOx storage/reduction process. The studies of the degradation mechanisms of the Pt/BaO/Al2O3 catalyst will direct the development of more efficient and stable NSR catalysts.

5. Development of NSR catalysts

The Pt/BaO/Al2O3 catalyst is the first generation NSR catalyst and significant NOx emission control has been achieved with this catalyst. However, to meet the more stringent NOx emission standards and realize broad implementation of this NSR technology, it is very urgent to develop low-cost, highly efficient and durable NSR catalysts. The development of next generation NSR catalysts is mainly focused on the improvements of precious metal components for higher NO oxidation and NOx reduction activity, NOx trapping components for higher NOx storage capacity and a wide storage window, and novel metal oxide supports with higher tolerance of sulfur poisoning and higher thermal stability. In the following section, we will give a detailed review of the recent development of NSR catalysts.

5.1 Precious metals

Pt is the most commonly used precious metal in the NSR catalysts. As discussed in the previous sections, Pt plays several key roles in the NOx storage/reduction cycles. However, in the literature, Pd and Rh were also used as the substitute of Pt metal for NSR catalysts. To combine the merits of different precious metals for the NOx storage/reduction reactions, bimetallic systems were also reported.

5.1.1 Monometallic system. Pd has been widely used as a key component in the three-way catalyst. 106,107 It shows excellent catalytic activity for both the oxidation of CO and hydrocarbons and the reduction of NOx under stoichiometric conditions. Recently, Pd has been investigated as an alternative to Pt for the NSR catalyst and it has been reported showing...
better performance than Pt for the NO$_x$ storage and reduction under some specific conditions.\textsuperscript{108-110} Meanwhile, Pd is a less expensive platinum group metal (PGM) with relatively high abundance compared with Pt. So the substitution of Pt with Pd can reduce the NSR catalyst cost and accelerate the application of NSR technology.

Salasce \textit{et al.}\textsuperscript{109} compared the NO$_x$ storage/reduction activity between Pd/BaO/Al$_2$O$_3$ and Pt/BaO/Al$_2$O$_3$ using lean-burn exhausts containing NO, O$_2$, C$_3$H$_6$ and N$_2$. As shown in Fig. 13, at 300 °C, the outlet NO$_x$ concentration over Pd/BaO/Al$_2$O$_3$ is lower than that over Pt/BaO/Al$_2$O$_3$. Therefore, Pd/BaO/Al$_2$O$_3$ shows a higher NO$_x$ storage capacity and better NO$_x$ reduction activity than Pt/BaO/Al$_2$O$_3$. Further XPS analysis revealed that the convertibility of Pd$^{2+}$ ↔ Pd during the lean and rich conditions contributes to its high NSR activity.\textsuperscript{108,110} At 300 °C, the NO$_x$ reduction during the rich cycle over Pt/BaO/Al$_2$O$_3$ is not complete possibly due to the self-poisoning of the reaction by adsorption of NO or C$_3$H$_6$ derived species (CO, carbonaceous species) onto Pt sites.\textsuperscript{111} However, when increasing operating temperature to 400 °C, BaO prevents the self-poisoning of Pt sites and at this temperature, Pt/BaO/Al$_2$O$_3$ shows slightly better NSR activity than Pd/BaO/Al$_2$O$_3$. Su \textit{et al.}\textsuperscript{111} also got similar results at relatively low temperatures when using hydrocarbons as reducing agents.

The NO$_x$ storage/reduction activity of monometallic Rh/Ba/Al$_2$O$_3$ catalyst was also studied by Breen\textsuperscript{112} and Abdulhamid\textsuperscript{113} \textit{et al.} Their studies showed that Rh has the highest NO$_x$ reduction activity among Pt, Pd and Rh, although the total NO$_x$ conversion on Rh is lower than the other two metal-based NSR catalysts. The low NSR activity of Rh/Ba/Al$_2$O$_3$ is due to its low NO$_x$ storage capacity as a result of its low NO oxidation activity.

5.1.2 Bimetallic system. Generally, it has been reported that Pt shows higher NO oxidation activity than Pd and Rh, whereas Pd and Ph show higher NO$_x$ reduction activity than Pt. Therefore, it is very interesting to investigate Pt–Pd and Pt–Rh based bimetallic NSR catalysts to achieve a higher overall NO$_x$ conversion.

As reported by Amberntsson \textit{et al.},\textsuperscript{79,114} the NO$_x$ trapping capacity and NO oxidation activity is lower for Pt–Rh/BaO/Al$_2$O$_3$ catalysts than Pt/BaO/Al$_2$O$_3$ catalysts. However, NO$_x$ reduction activity over the Pt–Rh/BaO/Al$_2$O$_3$ catalyst is better than that on the Pt/BaO/Al$_2$O$_3$ catalyst. Due to a higher NO$_x$ reduction activity on Rh regardless of sulfur poisoning, the combination of Pt and Rh into the NSR catalysts exhibits a better NO$_x$ storage/reduction performance than the monometallic Pt/BaO/Al$_2$O$_3$ catalyst.

Recently, Wang \textit{et al.}\textsuperscript{115} prepared a Pt/Co/BaO/Al$_2$O$_3$ catalyst by an impregnation method. The Pt/Co/BaO/Al$_2$O$_3$ catalyst showed better NSR activity and higher N$_2$ selectivity than the conventional Pt/Ba/Al$_2$O$_3$ catalyst. The studies revealed that the addition of Co not only accelerates nitrates/nitrates formation on Ba sites, but also improves NO$_x$ adsorption on Al sites. The intimate contact of Co with Ba/Al provides more active sites for NO adsorption, oxidation and desorption. In addition, the synergistic effect of Pt and Co may accelerate the NO$_x$ reduction.

5.2 NO$_x$ trapping components

BaO or Ba is the first investigated NO$_x$ storage material. However, the biggest drawback using BaO as NO$_x$ storage material is its poor resistance to sulfur poisoning toward synthesis of thermodynamically more stable BaSO$_4$ than Ba(NO$_3$)$_2$. Therefore, other alkaline and alkali metals have been extensively studied as NO$_x$ storage materials for NSR catalysts.

Kustov and Makkee\textsuperscript{116} studied the NO$_x$ storage/release performance on Ba/Al$_2$O$_3$, Sr/Al$_2$O$_3$, Ca/Al$_2$O$_3$ and Mg/Al$_2$O$_3$ using FT-IR spectroscopy coupled with mass spectrometry (MS). Fig. 14 shows the FT-IR spectra upon adsorption of 800 ppm NO in 20% O$_2$ in the He mixture on Al$_2$O$_3$, Ba/Al$_2$O$_3$, Sr/Al$_2$O$_3$, Ca/Al$_2$O$_3$ and Mg/Al$_2$O$_3$, respectively. The maximum NO$_x$ adsorption is observed on pure Al$_2$O$_3$ after ~5 minutes of contact. For supported Ba, Sr, Ca and Mg systems, most of the NO$_x$ is adsorbed within the first 20–30 min and the complete NO$_x$ sorption takes about 1–2 h. After the NO$_x$ adsorption was saturated, the flow of NO was stopped and desorption occurred in air with increasing temperature from 200 to 600 °C. The desorbed species were detected by MS, with NO$_x$ desorbed amount and storage capacity listed in Table 2. The NO$_x$ desorbed from Al$_2$O$_3$ is very little, which is not shown in Table 2. It is obvious that the NO$_x$ storage capacity increases from Ba to Ca with increasing basicity of the alkaline earth materials. For the Mg/Al$_2$O$_3$ system, the NO$_x$ storage is very low, which may be due to low thermal stability of trapped nitrates at a storage temperature of 200 °C. Except the Mg/Al$_2$O$_3$ system, most of the adsorbed NO$_x$ are released above 500 °C. However, for Ba and to some extent for Sr, trapped nitrates even will be stable at temperatures above 600 °C. The high thermal stability of Ba- and Sr-nitrates will decrease their NO$_x$ release amount at relatively low temperature and decrease the cyclic NO$_x$ storage activity.

To increase the Ba-based system’s storage activity at low temperature, a Ba–Mg-based system was investigated as a promising NO$_x$ storage system.\textsuperscript{117} When Ba was partially replaced by Mg, the Pt/Ba–Mg/Al$_2$O$_3$ catalyst showed better NO$_x$ storage capacity than the Pt/Ba/Al$_2$O$_3$ catalyst at 200 °C, while at higher temperatures (300 and 400 °C) the trend was
Fig. 14 FT-IR spectra upon adsorption of 800 ppm NO in 20% O₂ in He mixture on (a) Al₂O₃, (b) Ba/Al₂O₃, (c) Sr/Al₂O₃, (d) Ca/Al₂O₃, and (e) Mg/Al₂O₃ at 200 °C. Reproduced from ref. 115 with permission from Elsevier.
reversed. Therefore, the optimization of Ba and Mg composition in the NSR catalyst is important in order to obtain better NO\textsubscript{x} capacity at a wide temperature window. Meanwhile, the Ba–Mg system exhibited high resistance to the deactivation by SO\textsubscript{2}, which may be due to a synergistic effect between Ba and Mg and a better interaction with the Al\textsubscript{2}O\textsubscript{3} support.

Apart from the above discussed alkaline metals, alkali metal, such as K, is also widely used as a NO\textsubscript{x} storage component in NSR catalysts. Toops et al.\textsuperscript{118} studied the NO\textsubscript{x} trapping capacity on the Pt/K/Al\textsubscript{2}O\textsubscript{3} catalyst at 250 °C. They found that the addition of K to Pt/Al\textsubscript{2}O\textsubscript{3} increases the trapping capacity from 2.3 μmol NO\textsubscript{x} m\textsuperscript{-2} to 6.2 μmol NO\textsubscript{x} m\textsuperscript{-2}. Without K, the NO\textsubscript{x} is primarily trapped on Al\textsubscript{2}O\textsubscript{3} in the form of nitrates with monodentate, chelating and bridged forms. However, with the presence of K, the NO\textsubscript{x} is primarily trapped by K in a free nitrate ion. Büchel et al.\textsuperscript{119} found that their flame synthesized Pt/K/Al\textsubscript{2}O\textsubscript{3} can achieve over 80% NO\textsubscript{x} conversion at a temperature range of 300–400 °C. At 400 °C almost no NO\textsubscript{x} exhaust was detected in the 50 fuel lean/rich cycles. This superior performance resulted from a good K distribution in the catalyst and the amorphous nature of K species, which were obtained by the novel flame spray synthesis method. However, at temperatures higher than 400 °C, the NO\textsubscript{x} conversion decreased to around 60%. The sudden drop of NO\textsubscript{x} conversion is probably due to the partial crystallization of K\textsubscript{2}CO\textsubscript{3}. Meanwhile, this performance decrease cannot be recovered upon operation at low temperature (300 °C) again. This research also revealed that the novel catalyst synthesis method is very important to enhance the catalyst NSR performance.

5.3 Metal oxide supports

The metal oxide support performs a significant role in the NSR catalysts. It not only helps in dispersing the precious metals and the NO\textsubscript{x} storage materials but also helps in increasing the stability, sulfur resistance and NO\textsubscript{x} storage/reduction activity of the NSR catalysts. Al\textsubscript{2}O\textsubscript{3} has been widely used as a support for NSR catalysts. However, as discussed previously, BaO will react with Al\textsubscript{2}O\textsubscript{3} to form spinel BaAl\textsubscript{2}O\textsubscript{4} at temperature over 600 °C, which has been considered as one of the degradation pathways for the Pt/BaO/Al\textsubscript{2}O\textsubscript{3} catalyst.\textsuperscript{102} Recognizing the importance of the NSR catalyst support, different single oxide and mixed oxide supports have been developed as an alternative of Al\textsubscript{2}O\textsubscript{3} for NSR catalysts.

5.3.1 CeO\textsubscript{2}, ZrO\textsubscript{2} and Ce\textsubsuperscript{Zr1-x}O\textsubscript{2}. An important component in three-way catalysts, CeO\textsubscript{2}, plays several key roles in providing oxygen storage capacity and keeping high dispersion of precious metals.\textsuperscript{120} Recently, CeO\textsubscript{2} has been investigated as a support for NSR catalysts. CeO\textsubscript{2} is a good catalyst for the generation of H\textsubscript{2} via water-gas shift and/or hydrocarbon steam-reforming reactions, which has been evaluated to be helpful for the regeneration and desulfation of NSR catalysts.\textsuperscript{121} Meanwhile, the presence of CeO\textsubscript{2} can enhance the sulfur resistance of NSR catalysts, since CeO\textsubscript{2} can trap SO\textsubscript{2} to form cerium sulfate to protect the NO\textsubscript{x} storage component (e.g., BaO) from sulfur poisoning.\textsuperscript{122} In addition, CeO\textsubscript{2} also increases the thermal resistance of NSR catalysts.\textsuperscript{123}

Kwak et al.\textsuperscript{123} compared the sulfur resistance and thermal resistance of Pt/BaO/CeO\textsubscript{2} and Pt/BaO/Al\textsubscript{2}O\textsubscript{3} catalysts. As shown in Fig. 15, after sulfation with SO\textsubscript{2} at 250 °C, the NO\textsubscript{x} uptake on Pt/BaO/CeO\textsubscript{2} decreased from 60% to 43%, while that decreased from 48% to 23% on Pt/BaO/Al\textsubscript{2}O\textsubscript{3}. After desulfation at 600 °C, the NO\textsubscript{x} uptake on Pt/BaO/CeO\textsubscript{2} recovered to 46%, and recovered to 29% on Pt/BaO/Al\textsubscript{2}O\textsubscript{3}. The Pt/BaO/CeO\textsubscript{2} catalyst showed better sulfur resistance and regeneration performance than the Pt/BaO/Al\textsubscript{2}O\textsubscript{3} catalyst. To figure out the positive effect of CeO\textsubscript{2}, the Pt/BaO/CeO\textsubscript{2} and Pt/BaO/Al\textsubscript{2}O\textsubscript{3} catalysts after desulfation were characterized by XPS and TEM (Fig. 16 and 17). As shown in Fig. 16, after desulfation, there is less sulfur left on Pt/BaO/CeO\textsubscript{2} than that on the Pt/BaO/Al\textsubscript{2}O\textsubscript{3} catalyst. Therefore it was concluded that for the Pt/BaO/Al\textsubscript{2}O\textsubscript{3} catalyst, BaSO\textsubscript{4} is mostly transformed to BaS with little sulfur actually removed after desulfation. While for Pt/BaO/CeO\textsubscript{2}, the better sulfur resistance is not due to the sulfur trapped on CeO\textsubscript{2}, but the small-sized Pt on Pt/BaO/CeO\textsubscript{2} which suppresses SO\textsubscript{2} oxidation into SO\textsubscript{3}, and therefore hinders the formation of BaSO\textsubscript{4}. As shown by the TEM images (Fig. 17) of these catalysts after desulfation at
600 °C, it is clear that agglomeration of the Pt particles was observed on the Pt/BaO/Al₂O₃ catalyst, while no obvious Pt sintering effect on the Pt/BaO/CeO₂ catalyst was observed, which may be another reason why Pt/BaO/CeO₂ performs better than Pt/BaO/Al₂O₃ after high temperature desulfation.

Other explanations suggest that high water-gas shift activity of Pt/CeO₂ increases the H₂ concentration during the rich conditions, which helps remove sulfur at relatively low temperature from the unstable cerium sulfate.

Besides CeO₂, ZrO₂ is also investigated as an alternative support of Al₂O₃ for NSR catalysts. Piacentini et al. studied the NOₓ trapping capacity on ZrO₂ and Al₂O₃ based NSR catalysts. They found that Pt/BaCO₃/ZrO₂ presented a higher NOₓ trapping capacity than Pt/BaCO₃/Al₂O₃ at low Ba loading. While at higher Ba loading, the NOₓ trapping capacity on the two tested catalysts is similar.

Strobel et al. synthesized a series of Pt/Ba/CexZr1–xO₂ catalysts by a two-nozzle flame spray pyrolysis method. They found that the support composition (CeₓZr1–xO₂) strongly affected the NOₓ reduction activity of Pt. Higher Ce content favored the formation of Pt oxides, therefore lowered its NOₓ reduction activity and the total NOₓ conversion efficiency (Fig. 18). The NOₓ storage capacity of the Pt/Ba/CexZr1–xO₂ catalysts before and after CO₂ exposure was also evaluated, as summarized in Table 3. It is obvious that complete BaCO₃ recovery was achieved on CeO₂, whereas BaCO₃ was not reformed on ZrO₂ and only partly reformed on Ce–Zr mixed oxide. Therefore, as discussed above, further optimization of

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**Fig. 16** XPS data of sulfur 2p data for fresh and after desulfation at 600 °C of Pt/Ba/Al₂O₃ (a and c) and Pt/Ba/CeO₂ (b and d). Reproduced from ref. 122 with permission from Elsevier.

**Fig. 17** TEM images of Pt/Ba/CeO₂ (a) and Pt/Ba/Al₂O₃ (b) catalysts after desulfation at 600 °C. Reproduced from ref. 122 with permission from Elsevier.

**Fig. 18** (a) Outlet NOₓ concentration during a transient experiment for the as-prepared Pt/Ba/ZrO₂ and Pt/Ba/CeO₂ catalysts at 350 °C, and (b) NOₓ concentration as a function of temperature and support composition during the fifth lean-rich cycle (compare Fig. 21a). Reproduced from ref. 123 with permission from Elsevier.
Pt/Ba/CeO₂  No  51.8  77
Pt/Ba/Ce₀.₅Zr₀.₅O₂  Yes  62.2  92
Pt/Ba/ZrO₂  No  40.9  61
Pt/Ba/ZrO₂  Yes  6.6  10

* 1 h at 800 °C in 10% O₂/He followed by 1 h in 20% CO₂/He.

Relative amount of Ba involved in the storage process assuming complete Ba(NO₃)₂ formation.

Table 3  Amount of stored NOₓ and relative amount of Ba involved in the storage process during saturation experiments at 400 °C (compare Fig. 18b). Reproduced from ref. 124 with permission from Elsevier

In addition, the sulfur resistance and regeneration ability of the Pt/Ba/Ce₁₋ₓZrₓO₂ catalysts was also evaluated by some researchers.\(^{126}\) Pt/Ba/Ce₁₋ₓZrₓO₂ catalysts showed better sulfur resistance than Pt/Ba/Al₂O₃ catalysts. Meanwhile, the sulfates elimination under desulfation conditions was more efficient on Pt/Ba/Ce₁₋ₓZrₓO₂ than on the Pt/Ba/Al₂O₃ catalyst.

**5.3.2 TiO₂ and Al₂O₃–ZrO₂–TiO₂ solid solution (AZT).**

TiO₂ has been investigated as an alternative support of Al₂O₃ for NSR catalysts due to its high tolerance against sulfur poisoning. Yamamoto *et al.*\(^{127}\) studied the sulfur tolerance of a series of 1% Pt–10% M₂O₃/TiO₂ catalysts during the NOₓ trapping, where M = Li, Na, K, Cs, Sr and Ba. They found that in an SO₂-containing feed, the NOₓ sorption capacity was not affected over Pt–Li₂O/TiO₂ but significantly deteriorated on the other tested catalysts containing other sorbents.

In addition to the weak basicity of Li compared with other additives, the formation of Li₂TiO₃ over Pt–Li₂O/TiO₂ leads to instability of the sulfates on Pt–Li₂O/TiO₂, which facilitates desorption of sulfur-containing species at low temperature. However, in order to mitigate the drawbacks of TiO₂, such as the low thermal stability, low surface area and poor mechanical properties, the mixed oxides containing Al₂O₃, ZrO₂ and TiO₂ are evaluated as a novel support for NSR catalysts.

Imagawa *et al.*\(^{128,129}\) synthesized a nano-composite containing Al₂O₃ and ZrO₂–TiO₂ solid solution (AZT), which was used as the support for Pt/Rh/Ba/K/AZT NSR catalysts. As shown in Fig. 19, the particle size of ZrO₂–TiO₂ in the nano-composite was smaller than that in the physically mixed oxide at all the measured temperatures. The typical TEM images of the AZT nano-composite and physically mixed AZT catalysts were shown in Fig. 20. It was believed that Al₂O₃ particles act as a diffusion barrier to ZrO₂–TiO₂ particles in the nano-composite oxide to prevent the agglomeration of ZrO₂–TiO₂ particles. As shown in Fig. 21, after a thermal aging test at different temperatures, the AZT nano-composite based Pt/Rh/Ba/K/AZT catalyst had a larger amount of NOₓ storage and less amount of NOₓ release during the lean-rich cycle when compared with that of the physically mixed AZT based Pt/Rh/Ba/K/AZT catalyst. Especially at 400 °C, the NOₓ storage capacity in the AZT nano-composite based Pt/Rh/Ba/K/AZT catalyst was about twice that of the physically mixed AZT based Pt/Rh/Ba/K/AZT catalyst. In addition, better NOₓ storage performance after sulfur aging was observed on the AZT nano-composite based Pt/Rh/Ba/K/AZT catalyst (Fig. 22). The monolithic AZT inhibited the solid phase reaction of K with support materials and a high percentage of active K was maintained for NOₓ storage. Meanwhile, it was suggested that Ba could help prevent sulfur poisoning on K and facilitate the NOₓ storage.

As reported in the literature, other mixed metal oxides, such as MgO–Al₂O₃,\(^{130}\) MgO–CeO₂,\(^{131}\) MnOₓ–CeO₂,\(^{132}\) and Al₂O₃–CeₓZr₁₋ₓO₂,\(^{133}\) were also evaluated as supports for NSR catalysts, which exhibited some superior performance compared to the Al₂O₃ support.

In Section 5, we reviewed the recent development of NSR catalysts, focused on the improvement of precious metals, NOₓ storage materials and metal oxide supports. The newly developed NSR catalysts possessed improved NSR activity and/or good resistance to sulfur poisoning and thermal...
Pt, BaO and Al$_2$O$_3$, respectively. Compounds and novel metal oxide supports as substitutes of oxides, the mixed alkali and/or alkaline earth metal low-cost other PGMs or non-PGMs and suitable perovskite NSR catalysts can be achieved by utilizing the relatively future development of low-cost, highly efficient and durable NSR catalysts were addressed in detail, concentrating on the improvements over precious metals, NO$_x$ storage materials, and metal oxide supports.

Despite the first generation NSR catalyst (Pt/BaO/Al$_2$O$_3$) being quite successful in NO$_x$ emission control, new generation NSR catalysts with low-cost, high efficiency and durability are urgently needed to meet the ever rigorous NO$_x$ emission regulations and develop the NSR technology. Currently, there is a consensus on the five-step NSR mechanism (Section 2), however, the understanding of each step of the NSR mechanism is far from clear, especially the last three steps regarding the regeneration of NSR catalysts. A further investigation of the NSR mechanism for a better understanding should be carried out while in search for more efficient NSR catalysts. In addition, more efficient NO$_x$ trapping materials and support materials need to be developed to alleviate the sulfur poisoning and thermal degradation, which are two big problems that affect the long-term stability of the NSR catalysts. Furthermore, the development of new materials (e.g. perovskite oxide-based materials$^{8,134}$) as alternatives of precious metals is very promising to reduce the cost of NSR catalysts. Finally, a novel synthesis method and a novel structured NSR catalyst (e.g. 3-D structured catalysts$^{135-137}$) would help to increase the NSR activity, sulfur poisoning resistance, and thermal stability.

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**References**