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ARTICLE

Ceria-based catalysts for low-temperature selective catalytic reduction of NO with NH₃

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Selective catalytic reduction of NO with NH₃ (NH₃-SCR) is a powerful technique for abatement of NO_x from stationary sources, and the currently used VO_x/TiO_2-based catalysts are widely applicable for medium-temperature conditions, but not suitable for NH₃-SCR operated at low temperatures. Recently, low-temperature NH₃-SCR has attracted considerable attention owing to the vast demand in industrial furnaces and feature of energy-conserving. During the past years, a great many of studies have demonstrated that ceria-based catalysts are potential for low-temperature NH₃-SCR. Herein we summarize the recent advances in the application of ceria-based catalysts for low-temperature NH₃-SCR. The review begins with a brief introduction of the general guideline for low-temperature NH₃-SCR and the interaction between the reactants and CeO_2. The different roles of ceria as pure support/active species, bulk doping component and surface modifier are discussed. As well, the mechanistic investigations (active sites, intermediates, reaction mechanism) and SO_2/H_2O tolerance are emphasized. Lastly, the perspectives on the opportunities and challenges of ceria-based catalysts for low-temperature NH₃-SCR in future researches are presented.

1. Introduction

The fast urbanization and rapid development of industry have caused serious air pollution and stringent regulations are released with growing environmental awareness. It is generally considered that the air pollution is predominantly from combustion processes of fossil fuels in power plants, vehicles and other incineration processes. Among various air contaminants, nitrogen oxides (NO_x) are notable and known as the major causes of haze, photochemical smog, acid rain, ozone depletion and the greenhouse effect. As such, great efforts have being made to minimize NO_x emission (deNO_x) and three approaches are mainly used: pre-combustion, combustion modification and post-combustion techniques.[1] Both pre-combustion and combustion controls are helpful, but can only achieve a modest reduction of NO_x emissions. For applications required to achieve high NO_x reduction, post-combustion control has to be resorted.

Catalytic reduction is attractive among various post-combustion methods because of their low cost and high efficiency. DeNO_x of flue gases from stationary sources can be efficiently achieved by using the technique of selective catalytic reduction of NO with NH₃ (NH₃-SCR). Nowadays, large majority of industrial deNO_x is carried out by this technology and WO_3 (MoO_3) modified V_2O_5/TiO_2 are the current commercially used catalysts for NH₃-SCR in industry. However, some disadvantages are still existed in these catalyst systems, including: (1) V_2O_5 is easy to sublimate and shed in the using process, and further generates biological toxicity when it enters into the environment; (2) the operation temperature window is relatively narrow, and a large number of N_2O will form at high temperature; (3) the high-temperature thermal stability is very poor.[2-4] In order to overcome these problems, the catalyst can be installed downstream of the particulate collector and flue gas desulfurization, which requires catalysts that can work well around 200 °C or even lower. Moreover, in many industrial furnaces (*e.g.* cement plant), the flue gas temperatures are much lower than that of the power plant, making strong requirement for low-temperature NH₃-SCR. Therefore, substantial attention has been recently paid to NH₃-SCR catalysts operated at low temperatures.[5]

Cerium oxide has been the subject of numerous investigations in recent years due to its wide application in catalytic fields, such as three-way catalysis (TWC), catalytic wet oxidation, oxygen permeation membrane system, fuel cell process and photocatalysis.[6-10] It also attracts considerable attention in NH₃-SCR.[11-16] We search CeO_2 and SCR as keywords from 2009 to 2014 in *Web of Science*, and the citation report is shown in Figure 1. It is obvious that both the published articles and citations are increased year by year, indicating that ceria-based catalyst is a continuing research hotspot in NH₃-SCR application.

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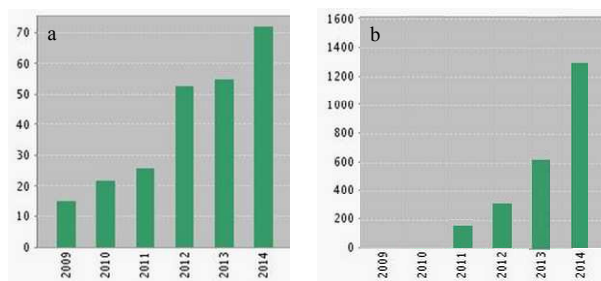[†] *These authors contribute equally.*

Fig. 1 The citation report in *Web of Science* about ceria-based catalyst in NH₃-SCR: (a) published articles and (b) citations in each year.

Owing to the favorable textural properties and strong ability to interact with other components, cerium oxide has been conventionally employed as the promoter or support in NH₃-SCR catalysts.[12, 17-19] This is very similar to TiO_2. With the study going further, researchers begin to realize that unlike TiO_2, this material can also be used as an active component,[20] which resembles V_2O_5. Despite these ever-increased understandings, a comprehensive summarization of the basic features of ceria-based catalysts in NH₃-SCR process and their structure-activity relationship is still lacking. In the present work, an overview of the ceria-based catalysts for low-temperature NH₃-SCR is given from the following aspects: the general guideline for NH₃-SCR catalysts operated at low temperatures, the interaction between ceria and the reactants, performance of different ceria-based catalysts, the active sites, intermediates and reaction mechanism, and finally the SO_2/H_2O tolerance. We hope that it can help researchers more deeply understand the characteristics of ceria-based catalysts in the related processes, and a valuable scientific reference can be provided for the optimization of existing catalysts and the design of novel catalysts.

2. General guideline for SCR catalysts operated at low temperatures

NH₃ adsorption and subsequent oxidative activation (*i.e.,* H-abstraction) are important for the SCR of NO. In addition to the surface properties of catalysts, NH₃ adsorption and activation are also influenced by the reaction temperatures. In general, a high reaction temperature is unfavorable to NH₃ adsorption but promotes H-abstraction of the adsorbed NH₃ or related intermediate species (such as -NH₃NO), and a low reaction temperature favors NH₃ adsorption but inhibits the activity of H-abstraction. This brings about different requirements for NH₃-SCR in different temperature ranges and therefore, regulation of a catalyst's acidity and redox properties with respect to reaction temperature is very important. For SCR reaction operated at low temperatures, acidity is necessary. If the acid sites of catalysts are extremely low or even absence, the reaction can not be fully initiated. However, in the case that the acid sites are sufficient, the adsorption ability seems to be no longer a question and the oxidation ability of catalysts plays a crucial role. In other words, when the initiation of the NH₃-SCR reaction is fulfilled (adequate acid sites, no special requirement for acid strength), upgrading the oxidation ability of catalysts tends to be the key point to enhance the low temperature SCR activity. In fact, similar

standpoints have also been proposed in literatures.[21,22] Previous study by Lietti *et al.*[23] has indicated that over V_2O_5-WO_3/TiO_2 the catalyst redox functions govern the catalytic reactivity in the low-temperature region, whereas the SCR reaction in the high-temperature region is likely controlled by the surface acid properties.

The importance of redox property of catalysts in low-temperature NH₃-SCR can be also reflected by shifting the reaction pathway from "standard SCR" (equation 1) to "fast SCR" (equation 2). Although for some catalysts, like Cu-SSZ-13, an inhibition effect on the low temperature activity can be found in the presence of NO_2 due to accumulation of NH_4NO_3,[24] it is widely reported that when certain amount of NO_2 coexists with NO, "fast SCR" occurred and the reaction rate can be significantly improved and thus greatly enhances the NO reduction performance.

$$4NH_3 + 4NO + O_2 = 4N_2 + 6H_2O \qquad (1)$$
$$2NH_3 + NO + NO_2 = 2N_2 + 3H_2O \qquad (2)$$
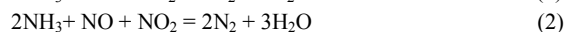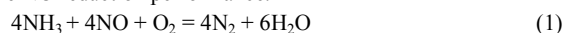
3. Interaction of ceria with the reactants

The selective catalytic reduction of NO by NH₃ in the presence of excess oxygen is a complex chemical process that predominantly occurs on the surface of solid catalysts, and for ceria-based catalysts, the interaction between ceria and the reactants, which comprises compositional (*e.g.*, surface adsorption, transformation of reactants) and structural (*e.g.*, electron transfer, surface reconstruction) aspects, is principal to understand the reaction. On one hand, to ascertain how ceria participates in this process, a first aspect to clarify is the effect that the reaction conditions have on the state of the ceria surface. On the other hand, to get insight into the role of ceria and obtain general guideline to design new efficient catalysts, one essential thing to recognize is the evolution of reactants on ceria surface. Hence, before providing a detailed summary of the varied ceria-based catalysts and their catalytic performances, a brief overview of the interaction between ceria and the reactants (NO, O_2, NH₃) is presented.

3.1 Interaction of ceria with NO

As is well known, ceria is an essential component in three-way catalysts (TWCs) developed for removal of NO from mobile source, and the interaction between NO and ceria has been widely studied during the last decades. With the aid of multiple spectroscopic characterizations and thermal analysis techniques, as well as theoretic calculations, the adsorption characteristics of NO on ceria are intensively monitored and insightful information has been obtained. In summary, the following features are recorded:
I) NO-ceria interaction is strongly dependent on the surface state of ceria and tends to take place at the surface oxygen vacancy of ceria. Defects in solid like steps, kinks and vacancies have been long considered as feasible sites for molecule adsorption due to their relatively large surface energy. By employing a plane-wave DFT study, Yang *et al.*[25] calculated the adsorption of NO on unreduced and reduced CeO_2 surfaces. The result shows that independent of the adsorption geometry and surface structure of ceria, the adsorption energy of NO on reduced ceria is nearly ten time larger than that on stoichiometric ceria (Table 1), revealing preferential interaction of NO with ceria in reduced state. Zhang *et al.*[26] studied the adsorption,

diffusion and reaction of NO molecules at reduced CeO_2 (110) by DFT+U calculations and demonstrated NO preferably adsorbed at the surface oxygen vacancy. By alternately forming NO_2 and dissociating into NO and O, the adsorbed NO could diffuse along any direction at the surface. Moreover, two NO molecules adsorbed at isolated vacancies could combine to form N_2O_2 dimer, which subsequently dissociated to give rise to N_2. More details are reported by Nolan.[27] They showed that on doped ceria surface with one oxygen vacancy, NO adsorption was weak and sit above a defective surface. Instead, adsorption of two NO molecules at neighboring vacancy sites resulted in strong adsorption and formation of a N–N-like bond, as well as lengthening of the N-O bonds.

Table 1 Adsorption energies (ΔE_{ad}, in kcal/mol) for $NO/CeO_2(111)$ and $NO/CeO_2(110)$ and the electron transfer (Δq, in e) between the surface and the molecule.[25]

Adsorption modes	ΔE_{ad}	Δq
NO on stoichiometric surface:		
atop-O on (111)	0.95	0.012
atop-Ce on (111)	2.33	-0.018
atop-Ce on (110)	3.09	-0.071
Cey-bridge on (110)	3.03	-0.033
Cey-bridge on (110): upright	4.13	-0.035
Cey-bridge on (110): tilted	5.54	-0.047
NO on O-vacancy of O-defected surface:		
(111)	41.9	-0.28
(110)	30.6	-0.39

II) Due to strong interaction between NO and CeO_2, dissociative adsorption of NO readily occurs on ceria, especially for nonstoichiometric ceria with reduced chemical valence. Luo et al.[28] studied the adsorption behavior of NO on ceria by TPD-MS and found that four kinds of species (NO, N_2, N_2O, O_2) were evolved during thermal desorption of NO. The appearance of NO desorption peak indicates molecular adsorption of NO on ceria while the detection of N_2, O_2 and N_2O suggests dissociative adsorption of NO. Martinez-Arias et al.[29] conducted an experiment of NO adsorption on CeO_2 pre-outgassed at different temperatures. It is revealed by EPR characterization that the NO adsorbed molecules are in radical form at -196 ^{o}C and could take in electrons trapped at stable oxygen vacancy generating diamagnetic products at 23 ^{o}C. Moreover, by correlating the amount of N_2O generated with the outgassing temperatures, their result indicates that the surface centers containing associated oxygen vacancies are the active sites for NO dissociation on ceria. As for NO_2, the case is similar. Nolan et al.[30] performed DFT calculations on the interaction of NO_2 with reduced ceria surfaces. They found that NO_2 bound with defective surface in such a way that one of the O-atoms occupied the vacancy site. The adsorbed molecule showed a bent configuration with O–N–O angle of ~113° and the N–O bond length involving the surface O-atom was significantly larger than that of the gas-phase N–O bond length in NO_2.

III) The interaction of NO with ceria can lead to generation of diverse N-containing surface species. According to literatures,

various N_xO_y species, such as gaseous N_2O, NO_2, N_2O_4, and surface adsorbed species, like azide (N_3^-), nitrosyl (NO), nitrosyl anion (NO^-), nitric oxide dianion (NO^{2-}), hyponitrite anions ($N_2O_2^{2-}$), nitrite ions (NO_2^-) and nitrate ions (NO_3^-), have been captured in the process of NO adsorption on ceria.[31] Apparently, the appearance of charged species provides solid evidence of electron transfer between NO and ceria.[25] Generally, there are several N-containing species coexisting on catalyst surface, and for certain species, the configuration can be varied, e.g., from mono-dentate, bi-dentate, chelating to bridging bonding. Moreover, the nature and distribution of these NO derived species are closely related with the surface oxidation state of ceria and the operation temperature. For example, Overbury et al.[32] investigated the chemisorption and reaction of NO on oxidized and reduced ceria surfaces. Nitrite and N_2O are seen on a fully oxidized surface while NO^-, N_2O, and dissociation products are observed on a reduced surface. The NO adsorption at -123 ^{o}C was predominantly molecular while exposing NO at 127 ^{o}C lead to a thermally activated nitride which desorbed at temperatures above 227 ^{o}C. Regarding the surface species-temperature relationship, it is commonly recognized that such surface N-containing species with low oxidation state like molecular NO and negative charged NO^- can be observed at relatively low temperatures, while such species with high chemical valence likes NO_2^-, NO_3^- are dominated at ambient or elevated temperatures.

Concerning the effect of NO-ceria interaction on the final catalytic performance, it is important to note that although the dissociative adsorption of NO is no longer considered as an imperative step for NO reduction in NH_3-SCR as that in three-way catalysis (TWC),[33] and the cover of surface nitrate species may bring some disturbances to NH_3 adsorption,[34, 35] the facile activation of NO on ceria can still show its significance in NH_3-SCR, especially in the low temperature range. On one hand, both the generation of NO_2 and the abstraction of H from adsorbed NH_3 are supposed to be key steps in low-temperature NH_3-SCR and the required oxidation process can be realized by the active O species derived from breaking of NO bond. On the other hand, according to the widely proposed Langmuir-Hinshelwood mechanism, the direct reaction between activated NH_3 and surface NO derived species, such as nitrite, is crucial to enhance the catalytic performance.[36] Thus, the unique role of ceria in NO adsorption and activation ought to play a positive role in the low-temperature NH_3-SCR.

3.2 Interaction of ceria with O_2

In standard NH_3-SCR reaction, O_2 is an indispensible reactant and previous studies have shown that although the reaction of $NO+NH_3$ can take place in the absence of O_2, the NO reduction efficiency is much inferior in comparison with the reaction of $NO+NH_3+O_2$.[37] Similar to NO, O_2 is prone to be activated on ceria due to its excellent oxygen storage capacity (OSC). The commonly reported surface activated oxygen species including superoxide (O_2^-), peroxide (O_2^{2-}) and they can be ultimately transformed into lattice oxygen (O^{2-}) at elevated temperatures. The generation of superoxide and peroxide species is supposed to be linked to the adsorption of O_2 on one- and two-electron defects, respectively.[38]

The promotional role of O_2 in NH_3-SCR is well-recognized and two general functions can be concluded. One is considered to be

related with the oxidation of reduced catalysts and closure of the reaction cycle. This is well depicted by Topsøe *et al.* in their mechanistic study of the reaction details.[39] In some cases, particularly at low temperatures, re-oxidation of catalysts is deemed to be the rate-determined step.[40] The other is connected with the oxidation of NO reactant, which speeds up the reaction via the "fast SCR" pathway. In comparison with lattice oxygen, the surface oxygen species can interact with NO more easily due to its higher mobility. As such, NO could be more easily oxidized to NO_2 or nitrate species, and then reacts with adsorbed NH_3 or NH_4^+ at low temperatures.[36, 41] Nevertheless, concerning the details of O_2-ceria interaction on the activation and transformation of N-containing species, limited information is available. Philipp *et al.*[42] conducted a comparison of NO adsorption and NO/O_2 co-adsorption on ceria by DRIFT spectroscopy. Their results show that NO adsorption is dominated by the formation of nitrite species (chelating nitrite, cis-hyponitrite, trans-hyponitrite), whereas co-adsorption of NO/O_2 leads to the formation of nitrates. For the specific role of oxygen, Hadjiivanov *et al.*[43] showed by experimental evidence that the addition of a small amount of O_2 to NO could lead to a rapid disappearance of the azide species, while the N-containing species were stable in the presence of NO or O_2 alone. They attributed the disappearance of azide to the interaction between N_3^- and NO_2, which likely followed the similar mechanism to that of coupling of NCO^- and NO_2 proposed for the reduction of NO_x with hydrocarbons.[44]

As oxygen is essential in SCR reaction, the ability of restoring and releasing oxygen of the catalyst is an important factor to determine the SCR activity. In this regard, ceria-based catalysts present an innate prospect because of the easier redox cycles from Ce^{4+} to Ce^{3+}.

3.3 Interaction of ceria with NH_3

Different from NO and O_2, NH_3 is a typical basic molecule, and accordingly the interaction of ammonia with ceria is largely dependent on the acid-basic property of ceria. It is well known that NH_3-solid interaction can lead to generation of two kinds of surface NH_3 species, *i.e.*, coordinated and protonated NH_3, which corresponds to Lewis and Brønsted acid sties, respectively. For Lewis acid, it can accept electron pair from NH_3 while for Brønsted acid, it can donate proton to NH_3 forming surface NH_4^+. Some author supposed that for NH_3-SCR, the protonation of ammonia was too weak as activation and needed for reaction of a highly oxidant species like NO_2. On the contrary, the coordination over high oxidation state cations gave rise to a highly reactive complex allowing reaction with NO.[33] However, confirmative evidences are lacking. Besides, it is important to note that although the binding forms of NH_3 with Lewis and Brønsted acid sites are distinctly different, no direct relation between the thermal stability of NH_3 and the type of acid sites can be correlated. In some catalyst systems, like V_2O_5/TiO_2, the coordinated ammonia was reported to be thermally more stable than protonated NH_3.[33, 45, 46] And in others, such as CuO/Al_2O_3, the protonated NH_3 was shown to be more thermally stable than coordinated NH_3.[47, 48] In fact, the acid sites are actually interchangeable with reaction conditions. The Lewis acid sites can be transformed into Brønsted acid after contact with stream forming surface OH group, and the condensation of OH groups at elevated

temperatures could change the Brønsted acid to Lewis acid.[49] From this point of view, the difference in NH_3 adsorption sites under the reaction conditions might not be fundamental, since H_2O is an indispensible product of NH_3-SCR.

Principally, both Lewis and Brønsted acid sites can be owned by ceria and originated from the cerium cations and surface H-terminated groups like OH, respectively.[50] Nevertheless, a variety of experimental results show that the acid sites of pure ceria are dominated by the Lewis type. For example, Wu *et al.*[51] studied the surface-dependent acid-base property of ceria nanocrystals via IR spectroscopy and found that irrespective of the ceria morphologies (cubes, octahedra, and rods), the signal of Lewis acid was evident while that due to Brønsted acid was absent. In Zaki's study,[52] they showed that the ceria prepared by calcination of $(NH_4)_2[Ce(NO_3)_6]$ exposed weak-to-moderate Lewis acid (cus Ce^{4+}) only, and the proton-donor hydroxyls (Brønsted acid sites) were not probed even with strong base molecules.

The acid strength constitutes another important aspect and more often than not, the activation of N-H bond is bound up with the acid intensity. For ceria, the acid-base property is reflected by its poor acidity. As revealed in literatures,[53, 54] the peak temperature of NH_3 desorption on ceria is in the range of 100-200 °C, implying weak interaction between NH_3 and ceria. Lavalley's study[55] showed that irrespective of the chemical state of ceria (*i.e.*, reduced or unreduced), the Lewis acid strength of cerium ions was weak. As well, by comparing the magnitude of upward shift of wavenumber on pyridine adsorption, they concluded that the Lewis acidity of ceria was inferior to that of ZrO_2 and TiO_2. Joshi *et al.*[50] carried out a theoretical investigation on NH_3-ceria interaction with both Lewis and Brønsted acid sites being considered. Their result showed that independent of the types of acid sites, the binding energy of NH_3 to acid sites was only in several kcal per mol. Cutrufello *et al.*[56] conducted a microcalorimetric experiment to explore the acidity of ceria and ceria-based solid solution. As revealed by the lacking of Q_{diff} (differential heat of adsorption) $\geq$ 80 kJ/mol, the result demonstrates that the acid strength of pure ceria is much weak. Besides, they showed that the chemical state of ceria (*i.e.*, reduced or unreduced) exerted an influence on the acid strength. That is, the acid sites are weakened after a reduction treatment, which can be explained by the fact that the charge/radius ratio of Ce^{3+} (radius 1.14 Å) is lower than that of Ce^{4+} (radius 0.97 Å).

It is obvious that NH_3 tends to adsorb on an acid surface and the stronger the surface acidity, the higher the adsorption of NH_3. When NH_3 adsorption is adequate, the state of NH_3 activation plays a crucial role. Thus, in addition to adsorption, the oxidation of NH_3 represents an important part of NH_3-ceria interaction. As depicted in section 2, the activation of ammonia is temperature-dependent. At low temperatures, partial dehydrogenation of NH_3 dominates the oxidation process. After abstracting one H atom from NH_3, surface NH_2 species is formed and it can readily react with NO forming intermediate NH_2NO species, and then decomposes into N_2.[57] As the temperature increases, over-oxidation of NH_3 gradually happens. Epling *et al.*[58] have shown that the NH_3-ceria interaction at high temperatures (> 350 °C) can lead to the unselective oxidation of NH_3. Irrespective of the operation temperatures (350, 400, 450 °C), N_2, NO and N_2O are the main products and the evolved concentration of NO is much higher than that of N_2O. As well, no

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NO_2 is detected in all cases. The over-oxidation of NH_3 can reduce the chance of NH_3 interaction with NO and is actually a side reaction of NH_3-SCR that should be avoided. In addition to reaction temperature, it is inherently controlled by the redox property of catalysts. If the catalyst is too oxidative, it can facilely detach all the three H atoms from NH_3 and consequently produces NO and N_2O.[59] In such circumstance, the introduction of acid sites to catalyst seems to be a good choice, since it is widely accepted that the acid sites can simultaneously help to reduce the ammonia oxidation and promote the ammonia adsorption on the catalyst.

From the above discussion, it is evident that the excellent redox property of ceria shows its advantage in low-temperature NH_3-SCR, but the inherently poor acidity of ceria constitutes the main obstacle for the reaction. Thus, the improvement of the acid property of ceria is necessary to its catalytic performance and such strategies like surface sulfation and introduction of foreign species with admirable acid property have been well recorded in literatures.[50, 54] Besides, it deserves to be noted that since the redox property is not independent with acid-base property and the introduction of acid sites will simultaneously lead to inhibition of the redox property, a proper balance between the acid-base property and redox property of the ceria-based catalysts needs to be regulated to achieve the optimal catalytic performance. In order to fulfill this requirement, the adequate choice of proper elements and careful control of the preparation parameters are needed.

4. Ceria-base catalysts for low-temperature NH_3-SCR

During the past years, considerable investigations have been carried out over ceria-based catalysts for NH_3-SCR. In general, the state of ceria in catalysts can be classified into three kinds according to their existence and using way. That is, surface modification, bulk doping and using as pure support/active component (Figure 2), following a "surface to bulk" sequence. Considering the fact that there are already some review papers covering the application of ceria in NH_3-SCR,[60-63] in this section, a comprehensive summary is omitted and attention is mainly paid on the characteristic points involved in the varied ceria-based catalyst systems for low-temperature NH_3-SCR.
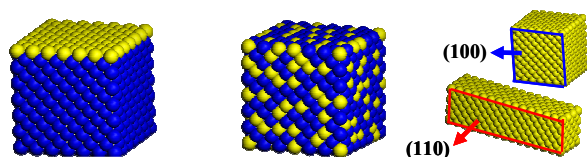

Fig. 2 Three using way of ceria in a heterogeneous catalyst. From left to right shows surface modification, bulk doping and using as pure support/active component. The yellow and blue spheres represent the atoms of ceria and other metal oxide, respectively.

4.1 Pure CeO_2 as active component or support

Pure CeO_2 usually exhibits poor NH_3-SCR activity. Guo et al.[64, 65] had investigated the calcination temperature and precursor effects on the catalytic performance of pure CeO_2 for selective catalytic

reduction of NO with NH_3. They found that pure ceria catalysts could not acquire full conversion of NO and the maximum value was obtained at 250 °C with ca. 80% NO conversion. Interestingly, Tang et al.[66] prepared CeO_2 via a controlled thermal decomposition of cerium oxalate and found that the material with homogeneous worm-like mesopores exhibited distinct activity in NH_3-SCR, with best activity reaching 100% NO conversion in the temperature of 275-425 °C. Li and co-workers[53] prepared a series of ceria catalysts with sulfate and nitrate precursors by hydrothermal and precipitation methods. Among them, CeO_2 catalyst prepared by hydrothermal method with cerium (IV) sulfate as a precursor showed excellent SCR activity and high N_2 selectivity in the temperature range of 230-450 °C. Similar result was reported by Yang et al.[67] in hydrothermal preparation of ceria from cerium nitrate with addition of pyrophosphoric acid. In these two cases, the activity enhancement was attributed to the increased acidity introduced by the sulfate and polyphosphate ions.

To further improve the activity of ceria, researchers are trying to use ceria as a support to deposit active components. In this case, ceria is potential to not only play the role of dispersing active species but also modulate the electronic and redox properties of surface dispersed species. As well, certain synergism in the interfacial region could be expected, consequently contributing the outstanding performance. Xu et al.[19] reported that by depositing MnO_x onto CeO_2 with a deposition-precipitation (DP) method, the obtained catalyst showed superior catalytic activity at low temperatures. Nearly 100% NO conversion was reached across the whole temperature region evaluated (80-150 °C). Similarly, other CeO_2-based supported catalysts (VO_x,[68] WO_3,[69] NiO[70]) were developed to approach the low temperature requirement. The above-mentioned studies are mainly about single metal-oxide supported catalysts. With the deepening of investigations, researchers begin to explore CeO_2 supported dual or even multiple metal-oxide catalysts. Zhu et al.[71] prepared a series of ceria supported bimetallic oxides (Ni-Mo, Cu-Ni and Fe-Mo) catalysts and investigated their catalytic performance in NH_3-SCR. It was revealed that the addition of NiO, CuO and Fe_2O_3 to MoO_3/CeO_2 catalysts led to different structures of surface molybdena species, i.e., isolated regular tetrahedral, highly distorted tetrahedral and polymerized octahedral molybdena species, and the intensities of interaction between molybdena species and these metal oxides exhibited the same order with the surface acid intensities of the Lewis acid sites. As such, the reactivity was deduced to be tightly related to acid properties of the catalysts.

In addition to surface dispersed species, the property of ceria support constitutes another important factor influencing the final catalytic performance. The rapid advancement in material science has enabled us to fabricate ceria with different structures and morphologies.[72-74] Nevertheless, in contrast to the vast investigations in such reactions as CO oxidation and water-gas shift (WGS), the exploration of special structured ceria as catalyst support in NH_3-SCR is much less reported.[70]

It is important to note that the using of pure ceria as active component or support is convenient to study the structure-activity relationship of ceria-based catalysts in NH_3-SCR. However, from the viewpoint of activity improvement, the employment of pure ceria as active component is not advocated. In the case of foreign component introduced, it is commonly recognized that to achieve the maximum

activity, sufficient contact between ceria and other component is needed. In this regard, the adoption of ceria as catalyst support seems to be not favorable.

4.2 Ceria-based mixed oxides (bulk doping)

In comparison with ceria-based supported catalysts, the using of ceria-based mixed oxide catalysts for NH_3-SCR is dominant. Actually, bulk modification of CeO_2 is a common means to improve the catalytic performance and thermal stability. The properties of CeO_2 can be modulated by the addition of appropriate oxides so as to obtain binary or multivariate solid solutions, spinel, perovskite oxides, or mixed oxides. In composite oxide catalysts, one metal element can modify the catalytic properties of another, which results from both electronic and structural influences. After bulk modification of CeO_2, these composite oxides can be as supports (*e.g.*, CeO_2-ZrO_2, CeO_2-SnO_2) or directly as catalysts (*e.g.*, CeO_2-TiO_2, CeO_2-MnO_x), which are increasingly attractive for their high activity.

Although MnO_x-CeO_2 catalyst was earlier investigated in NO_x sorption and NO reduction by H_2,[75-77] until 2003, Qi *et al.*[78] present the first study on NO reduction by NH_3 using mixed MnO_x-CeO_2 catalysts. Their results show that MnO_x-CeO_2 is a superior catalyst for NO reduction by NH_3 in the low temperature window of 80-150 ^oC with 100% N_2 selectivity and complete NO conversion at temperatures as low as 120 °C. Several years ago, Gao *et al.*[79] prepared Ce-Ti mixed-oxide catalysts by a sol-gel method. The most active catalyst was obtained with mass ratio of CeO_2/TiO_2 equaling to 0.6. Thereafter, CeO_2 mixed with TiO_2 has been extensively reported,[80, 81] and numerous types of CeO_2-containing catalysts were developed by researchers, including Ce-W, Ce-Nb, Ce-Sn, Ce-Cu, Ce-Mo and Ce-Ta.[35, 82-86]

Analogue to the research for supported catalysts, the development of ceria-based mixed oxide catalysts with multiple components is attempted and proved to be an effective way to enhance the activity and extend the temperature window of catalysts in NH_3-SCR. Liu *et al.*[87] reported the preparation of Cu-Ce-Ti oxide by a hydrothermal method and found the ternary component catalysts displayed much better activity than the binary Cu-Ti and Ce-Ti oxide catalysts. The best activity was acquired by $Cu_{0.1}Ce_{0.1}Ti_{0.8}O_x$, with more than 70% NO conversion at 150 ^oC and nearly full NO conversion at temperature between 200-350 ^oC under gas hourly space velocity GHSV of 64000 h^{-1}. The formation of dual redox cycle ($Cu^{2+} + Ce^{3+} = 2Cu^+ + Ce^{4+}$, $Cu^{2+} + Ti^{3+} = 2Cu^+ + Ti^{4+}$) was supposed to play key roles for the superior catalytic deNO$_x$ performance. Similar result was also observed in Mn-Ce-Ti oxide system.[88] Chen *et al.*[89] revealed that CuO-CeO_2-TiO_2 ternary oxide catalyst owned excellent NH_3-SCR activity in a low-temperature range of 150-250 °C. They depicted that the interactions between copper, cerium and titanium oxides lead to high dispersion of metal oxides with increased active oxygen and enhanced catalyst acidity, and a synergistic effect on the activation of reactants was proposed based on the results of DRIFTS (Figure 3). Yu *et al.*[90] prepared Ce-Sn-Ti mixed oxides catalyst by an inverse co-precipitation method and an obvious promotional effect of SnO_2 was found. The Ce-Sn-Ti catalyst was much more active than Ce-Ti and the best Ce:Sn molar ratio was 2:1. Characterization results revealed the introduction of SnO_2 could

result in not only higher specific surface area, larger pore volume and poorer crystallization, but also greater conversion of Ce^{4+} to Ce^{3+} and increased amount of chemisorbed oxygen, which were beneficial to improve the NH_3-SCR activity.
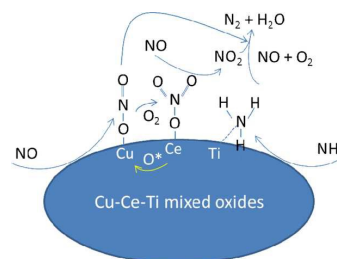

Fig. 3 Schematic illustration of the NH_3-SCR reaction on CuCeTi catalyst at low temperatures.[89]

It is well known that the preparation process is very important to the activity of catalysts. Thus, the influence of preparation parameters, such as preparation method and calcination temperature, on the catalytic performance of NH_3-SCR has been investigated systematically.

Methods commonly used to prepare composite oxide catalysts including co-precipitation, citric acid method, sol-gel, hydrothermal and homogeneous precipitation. Homogeneous precipitation, characterized by a highly uniform increase in the pH of metal salts solution achieved by thermal decomposition of some organic alkali, is suitable to produce highly dispersed mixed metal oxides. Shan *et al.*[91] prepared a $CeTiO_x$ mixed oxide catalyst by a homogeneous precipitation method. The catalyst showed much higher NH_3-SCR activity than the supported CeO_2/TiO_2 catalyst, with significantly improved resistance to high space velocity. The homogeneous precipitation method was also used in other catalyst systems, such as CeO_2-MoO_3,[35] CeO_2-WO_3,[82] CeO_2-VO_x.[92] Sol-gel method is alternative to prepare mixed oxide catalysts with highly dispersed species and nano-scale oxides in the structure. Gao *et al.*[93] prepared CeO_2-TiO_2 catalysts by three methods, and results indicated that the catalyst prepared by a single step sol-gel method had the highest NH_3-SCR activity. High surface area and good redox properties are important for catalytic activity, and the strong interaction between Ce and Ti as well as high concentration of amorphous or highly dispersed nano-crystalline ceria could explain the excellent performance of the catalyst prepared by single step sol-gel method. However, the case is not always the same. Liu *et al.*[94] reported that cerium-tungsten oxide catalysts prepared by impregnation and solid processing methods exhibited better NH_3-SCR activity than that prepared *via* the sol-gel method in 175-500 °C.

In practical utilization of NH_3-SCR, the temperature is not constant and may suffer sudden increase in some working conditions, possibly resulting in structural change and activity variation of catalyst. Therefore, it is very necessary to investigate the influence of calcination temperature on catalyst, which is also important for the further catalyst molding in practical use.[85, 95-97] Wang *et al.*[95] studied the effect of calcination temperature on the structure and catalytic performance of $CeMoO_x$ mixed oxide catalyst in SCR of NO_x with NH_3. The $CeMoO_x$-400 sample shows high NH_3-SCR activity with NO_x conversion of 100% in the temperature

range 175-375 °C. Compared to CeMoO$_x$-400, sample CeMoO$_x$-500 shows an activity with slightly lower NO$_x$ conversion below 200 °C, but higher NO$_x$ conversion above 350 °C. However, further increase of the calcination temperature leads to the noticeably drop of the NO$_x$ conversion below 250 °C.

In addition to influence of preparation parameters, recently the morphology effect of composite oxide catalysts on the catalytic properties attracts much attention, and some interesting results have been obtained. For instance, Jiang et al.[98] prepared hollow and solid MnO$_x$-CeO$_2$ nanospheres with a supercritical anti-solvent process. Activity tests indicate that the hollow MnO$_x$-CeO$_2$ exhibits better NO conversion at low temperatures, which is attributed to the higher surface area, better oxygen mobility and richer surface active oxygen species.

Ceria-based composite oxides are also employed as support for NH$_3$-SCR catalysts. By adding zirconium oxide into ceria, the oxygen storage capacity (OSC) and thermal stability of CeO$_2$ are significantly improved. This leads to CeO$_2$-ZrO$_2$ being investigated as a suitable NH$_3$-SCR catalyst support in some detail by several researchers. Li et al.[18] deposited six transition metal oxides (WO$_3$, MoO$_3$, Mn$_2$O$_3$, CrO$_3$, Fe$_2$O$_3$ and Co$_2$O$_3$) on CeO$_2$-ZrO$_2$ and their catalytic activities were tested. Among these catalysts, WO$_3$/CeO$_2$-ZrO$_2$ catalyst showed the highest conversion efficiency due to the synergetic effect between tungsta and ceria-zirconia. Shen et al.[99] investigated the effect of Ce-Zr on NH$_3$-SCR activity over MnO$_x$/Ce$_{0.5}$Zr$_{0.5}$O$_2$ at low temperature. The experimental and kinetic model results indicated that the MnO$_x$/Ce$_{0.5}$Zr$_{0.5}$O$_2$ catalyst displayed high N$_2$ selectivity and good resistance to H$_2$O and SO$_2$. The apparent activation energy of the MnO$_x$/Ce$_{0.5}$Zr$_{0.5}$O$_2$ catalyst was 18 kJ mol^{-1}, which was much lower than that of MnO$_x$/TiO$_2$ (i.e., 38 kJ mol^{-1}). Gao et al.[100] prepared three different shapes (rod, cube, and polyhedral) of ZrO$_2$-CeO$_2$ to disperse manganese oxides. They found that MnO$_x$/ZrO$_2$-CeO$_2$ nanorods achieved significantly higher NO conversion than that of nanocubes and nanopolyhedra, attributed to the higher Mn^{4+} species, adsorbed surface oxygen and oxygen vacancies were associated with their exposed (110) and (100) planes.

Our research group has also carried out some investigations on the using of ceria-based composite oxide supports for low-temperature NH$_3$-SCR.[101, 102] Anatase TiO$_2$, CeO$_2$-TiO$_2$ solid solution, and CeO$_2$ were synthesized and used as supports to prepare CuO/TiO$_2$, CuO/CeO$_2$-TiO$_2$, and CuO/CeO$_2$ catalysts. The catalytic performances showed the following sequence: CuO/CeO$_2$ < CuO/TiO$_2$ < CuO/CeO$_2$-TiO$_2$.[101] Based on the characterization techniques, plausible explanations were given for the enhanced activities obtained by the mixed oxide supported catalysts: (1) the incorporation of Ce^{4+} into the lattice of anatase TiO$_2$ leads to the formation of unstable distorted octahedral coordination structure of Cu^{2+} in CuO/CeO$_2$-TiO$_2$ catalyst, which promotes the reducibility of copper species; (2) the enhancement of the electron interaction between copper oxide species and CeO$_2$-TiO$_2$ support through the redox cycles of Cu^{2+} + Ce^{3+} ↔ Cu$^+$ + Ce^{4+} and Cu^{2+} + Ti^{3+} ↔ Cu$^+$ + Ti^{4+}, which are beneficial to the formation of more Lewis acid sites on the surface of CuO/CeO$_2$-TiO$_2$ catalyst and the activation of reactant molecules to generate more NH$_4$NO$_2$ species.

4.3 CeO$_2$ as surface loading component (surface modification)

Ceria dispersed on other support with sufficient surface area, which can be viewed as the inverse configuration of ceria-supported catalysts, constitutes one of the most important kinds of ceria-based catalysts and has attracted considerable interest, owing to the merits of providing huge surface to separate the active phase, supplying unique environment for the reactions to take place and more importantly, constructing certain synergistic sites for activation of reactants.

Conventional carriers like TiO$_2$, Al$_2$O$_3$, and SiO$_2$ have been applied to support ceria for low-temperature NH$_3$-SCR. Among them, TiO$_2$ is most widely reported because of its nontoxicity, biological and chemical inertness, poor interaction with SO$_2$ and easy availability. Xu et al.[103] firstly prepared CeO$_2$/TiO$_2$ catalyst with CeO$_2$ as the main active component by using impregnation method. High activity and excellent N$_2$ selectivity were observed in the temperature range of 275-400 °C. Wang et al.[104] introduced CeO$_2$ into the tubular channels of titanium nanotubes (TNTs) for SCR application. In comparison with the catalysts supported by TiO$_2$ nanoparticles, the confined ceria showed superiority in NH$_3$-SCR due to the improved redox potential and special adsorption of NH$_3$. They also controllably fabricated two catalysts with ceria nanoparticles deposited inside and outside the TNTs.[105] Titanate nanotube confined CeO$_2$ catalyst showed remarkable resistance to alkali metal poisoning. Wang et al.[106] investigated the impact of TiO$_2$ exposed facets on the catalytic performance of CeO$_2$/TiO$_2$ in NH$_3$-SCR. They found that compared with TiO$_2$ support with dominate (101) facets, the using of TiO$_2$ with (001) facet yielded remarkably high activity for NO removal. The unique feature of active-energy (001) facets enhanced the thermal stability of CeO$_2$ whilst the presence of Ti^{3+} over TiO$_2$ surface effectively facilitated the SCR process, both of which resulted in the remarkable catalytic performance for the catalyst. Nevertheless, CeO$_2$/TiO$_2$ catalysts commonly suffer from insufficient activity at low temperatures. Shu et al.[107] investigated the effect of iron additives on the catalytic performance of the CeO$_2$/TiO$_2$ catalyst for NH$_3$-SCR. They found that the addition of iron could enhance the low-temperature activity and SO$_2$-poisoning resistance of the CeO$_2$/TiO$_2$ catalyst. Characterization results revealed that the addition of iron resulted in more Ce^{3+} and chemisorbed oxygen on the catalyst surface, thus increasing the amount of Brønsted acid sites and in situ formed NO$_2$, respectively.

Carbon materials, such as active carbon and carbon nanotubes, have also been used as high surface area, high pore volume supports, which leads to highly dispersed active sites beneficial for the NH$_3$-SCR reaction. Additionally, carbon is reported to exhibit unique property in decreasing the decomposition temperature of NH$_4$NO$_3$ and NH$_4$HSO$_4$, which is conducibe to enhance the low-temperature activity and SO$_2$ tolerance.[108, 109] Carbon materials usually need to be treated by pre-activation to improve catalytic performance. Chen et al. prepared cerium oxide supported on nitric acid-treated carbon nanotubes (CNTs) and NO conversion of more than 70% was obtained in the temperature range of 250-400 °C.[110] The activity of CeO$_2$/CNTs was attributed to the enlarged surface area created by HNO$_3$ treatment and suitable crystal size of CeO$_2$. In order to prepare highly dispersed nanoparticles on CNTs, Fang et al.[111] introduced a pyridine-thermal route to in situ disperse CeO$_2$ on CNTs for NH$_3$-SCR. Compared with the catalysts prepared by

impregnation or physical mixture methods, the catalyst prepared by the pyridine-thermal route presents the best NH$_3$-SCR activity. Activated carbon fiber (ACF) has been also applied as a catalyst support for removing the pollution sources due to their special characteristics. Lu *et al.*[112] investigated the catalytic activity of 10-40% CeO$_2$/ACF at different temperatures and the catalytic stability at 200 ^{o}C. The results show that the 10% CeO$_2$/ACF can yield higher NO conversion and maintain higher catalytic activity at higher temperature than others. Zhu *et al.*[113] modified ACF by low-temperature oxygen plasma and nitric acid, which were named as ACFP and ACFN respectively. The experimental results showed that the surface modification of ACF by low-temperature oxygen plasma and nitric acid could both greatly improve the conversion of NO, and CeO$_2$/ACFN showed better activities when compared to CeO$_2$/ACFP catalyst.

Zeolite catalysts have received much attention in recent years due to their enriched acidity and thermal stability, and many metal ion exchanged zeolites were reported to be active in NH$_3$-SCR reaction, such as Fe/SSZ-13,[114] Cu/SAPO-34,[115] Mn/NaY,[116] and Ce/ZSM-5.[117] Recently, SCR catalysts based on chabasite-type zeolites (*i.e.*, SSZ-13, SAPO-34) have been reported for NH$_3$-SCR with much improved activities and high thermal durability, and have received substantial attention.[114, 115] Among such a wide family of catalysts, iron and copper zeolites are particularly interesting and have been extensively studied, whereas there were relatively few reports about ceria as an active component supported on zeolites. This is attributed to the loss in the crystallinity degree of Ce-exchanged zeolites during exchange process and the probability of forming CeO$_2$ segregates appear as clusters after calcination.[118] Ce-zeolite catalysts for SCR of NO$_x$ with NH$_3$ were generally prepared by aqueous ion exchange (IE) procedure[117] and it is not possible to obtain high ion-exchange percentage of Ce^{3+}. IE of Ce^{3+} often results in CeO$_2$ along with other cations in the zeolite, which affects the catalytic activity to different extent, resulting in unpredictable NO$_x$ conversions. Instead, Kooten *et al.*[119] found that Ce-NaZSM-5 catalysts prepared by solid-state ion exchange showed superior NO$_x$ conversion in NH$_3$-SCR. It is also shown that high NH$_3$-SCR activity can be achieved over the physical mixture of CeO$_2$ and zeolite.[20]

It is seen from the above-mentioned studies that ceria can be used as an active species dispersed on the surface of catalysts. Also, cerium oxide is often used as an additive to modify the surface of catalysts. The addition of ceria could not only increase the activity but also play a stabilization role, enhancing the catalyst's SO$_2$/alkali resistance. Chen *et al.*[120] systematically investigated the effect of Ce on V$_2$O$_5$-WO$_3$/TiO$_2$ with low vanadium loadings for NH$_3$-SCR. The results indicated that Ce addition could enhance the NO$_x$ adsorption and accelerate the NH$_3$-SCR reaction due to the synergetic interaction among the Ce and V, W species. Ce mainly existed in the form of Ce^{3+} oxide in the catalysts, which was beneficial for the oxidation of NO to NO$_2$. Moreover, ceria additive on V$_2$O$_5$-WO$_3$/TiO$_2$ could provide stronger and more active Brønsted acid sites, which were beneficial for the NH$_3$-SCR reaction.

For supported ceria-based catalysts, some interesting results were obtained in our recent investigation.[121] We prepared a series of CeO$_2$/Ti$_x$Sn$_{1-x}$O$_2$ samples to investigate the effect of doping SnO$_2$ into TiO$_2$ for NH$_3$-SCR. The results of catalytic test suggested that NO removal efficiency of CeO$_2$/Ti$_{0.5}$Sn$_{0.5}$O$_2$ was higher than that of

CeO$_2$/TiO$_2$, particularly at low temperatures. Characterization results revealed that the introduction of SnO$_2$ resulted in the formation of rutile-type Ti$_{0.5}$Sn$_{0.5}$O$_2$ solid solution with larger specific surface area and better thermal stability. The interactions between CeO$_2$ and Ti$_{0.5}$Sn$_{0.5}$O$_2$ support could improve the redox performance of the catalyst, which was beneficial to the enhancement of catalytic activity. Furthermore, doping SnO$_2$ enhanced the surface acid sites and weakened the adsorption of nitrates, which played an important role in the catalytic reaction process.

5. Active sites, intermediates and reaction mechanism of ceria-based catalysts in low-temperature NH$_3$-SCR

Rational design of NH$_3$-SCR catalysts is of paramount importance to the advancement of NH$_3$-SCR technique, and this relies heavily on the understanding of such fundamental aspects like the nature of active sites, intermediates and reaction mechanism. In general, L-H and E-R mechanisms are two of the most accepted mechanisms proposed for NH$_3$-SCR. However, for different catalytic systems or even the system with exactly the same composition, varied hypotheses regarding on the active sites and the key intermediates have been proposed. Moreover, it is important to note that compared with the conventional V$_2$O$_5$/TiO$_2$-based catalysts, these issues in ceria-based catalysts are much less studied, and till now no consensus has been achieved.

Considering the fact that a vast number of ceria-based catalysts have been reported for low-temperature NH$_3$-SCR, we will discussed in the following part from three representative catalyst systems, *i.e.*, MnO$_x$/CeO$_2$, CeO$_2$/TiO$_2$ and WO$_3$/CeO$_2$. The choosing of them is mainly based on two considerations. Firstly, they belong to the most widely studied ceria-based catalysts for low-temperature NH$_3$-SCR. Secondly, distinctly different characteristics are exhibited by them. Commonly, the combination of MnO$_x$ with ceria does not change the type of acid sites, but obviously increases the amount of acid sites and improves the redox property, consequently displays extremely high NO conversion but inferior N$_2$ selectivity. In contrast, the combination of ceria with WO$_3$ hardly promotes the redox property of ceria.[59] Instead, the acid sites are greatly increased and more importantly, Brønsted acid appears with significant strength and quantity. This confers the catalysts excellent N$_2$ selectivity and much broader temperature window, but the activity in low temperature range is less prominent. The case of CeO$_2$/TiO$_2$ is just between MnO$_x$/CeO$_2$ and WO$_3$/CeO$_2$. That is, the combination of TiO$_2$ with ceria leads to generation of large quantity of Lewis acid sites and minor Brønsted acid sites.

5.1 MnO$_x$/CeO$_2$ system

MnO$_x$/CeO$_2$ is famous for its outstanding low-temperature NO reduction performance and thus attracts substantial interest. Yang *et al.*[122] conducted a steady-state kinetics study on MnO$_x$/CeO$_2$ and found that the low-temperature NH$_3$-SCR reaction was zero order with respect to NH$_3$ and first order with respect to NO. Besides, a mechanistic pathway was subsequently proposed by them based on the results of the single- and co- adsorption of reactants on MnO$_x$/CeO$_2$.[123] Similar with pure ceria, only Lewis acid sites are

observed on MnO_x/CeO_2. As well, amid (-NH_2) species are found after NH_3 adsorption on MnO_x/CeO_2. Thus, it is suggested that the reaction mechanism involves the initial NH_3 adsorption onto the Lewis acid sits, and then the formation of NH_2 species, followed by reaction between NH_2 and NO to produce N_2 and H_2O. This is essentially in accordance with the amide-nitrosamide mechanism typically reported for V_2O_5/TiO_2 catalysts.[124]

Shi *et al.*[19] proposed a reaction mechanism of MnO_x/CeO_2 catalysts based on the results of *in situ* DRIFTS and mass spectroscopy and it is shown in Figure 4. Similar with Yang's report, it is suggested that during the SCR reaction, gaseous NH_3 molecules are quickly adsorbed onto the Lewis acid sites. However, the mechanism follows an L-H type since NO molecules are adsorbed to generate NO^- species and then react with activated NH_3 to form the intermediate [NH_3· · ·NO^-]. This activated complex then decomposes to yield the reaction products, N_2 and H_2O, following transfer of H to the catalyst surface. Gaseous O_2 reoxidizes the surface to regenerate the active site and close the catalytic cycle. Moreover, they pointed out that since the decomposition process with the reduction of catalyst surface did not proceed at low temperatures, this reaction was the rate limiting step.
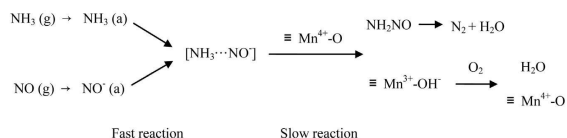

Fig. 4 Proposed reaction mechanism of MnO_x/CeO_2 catalyst in low-temperature NH_3-SCR.[19]

Baiker *et al.*[125] made a study on the relation between adsorption, redox and catalytic behavior of Mn-Ce mixed oxides in NH_3-SCR. By a pulse thermal analysis, they pointed out that NO_x and NH_3 were separately adsorbed on oxide sites, and no interference was observed as indicated by the similar uptakes of consecutive and separate adsorption of the two reactants. Unfortunately, detailed attributions of the separate adsorption sites are not given further. Mechanistic investigations by changing the sequence of admittance of reactants (NO_x, NH_3) indicated that at 100-150 °C nitrogen formation follows the E-R mechanism, where adsorbed ammonia reacts with NO_x in the gas phase, and adsorbed NO_x showed no significant reactivity.

Zhang *et al.*[126] compared the differences between pure CeO_2 and MnO_x/CeO_2 in NO adsorption and disclosed the reaction details of MnO_x/CeO_2 catalysts in NH_3-SCR with the aid of DFT calculation. They found that the adsorption energy of NO over MnO_x/CeO_2 was about 3-fold of that over CeO_2. NO favorably adsorbed at the oxygen (O*) adjusted Mn atom and elongated the Mn-O* bond length significantly from 2.07 to 3.31 Å, whereas the corresponding Ce-O* bond length in CeO_2 complex with adsorbed NO was only elongated by 0.44 Å. As a result, the adjusted O* of the Mn-O* bond in MnO_x/CeO_2 catalyst surface left to form a stronger nitrite intermediate (NOO*), in contrast to the adjusted O* of the Ce-O* bond in CeO_2. Moreover, the partial charge of nitrogen involved in nitrite formation was 0.143 e more positive over the MnO_x/CeO_2 surface than over the CeO_2 surface. Thus, the nitrogen atom during nitrite formation over the MnO_x/CeO_2 catalyst surface was a stronger

electrophilic site and could rapidly react with NH_3. This resulted in a higher NO conversion efficiency at low temperatures. In their opinion, the NH_3-SCR reaction over MnO_x/CeO_2 catalysts process corresponds well to the L-H mechanism.

For MnO_x/CeO_2 catalysts, N_2 selectivity is an important issue because more often than not, significant amount of N_2O is observed in the final products. Yang *et al.*[127] proposed that reaction between NH_3 and surface nitrate caused the generation of N_2O. Wu *et al.*[128] studied the promotional effect of Ca addition on the N_2 selectivity of MnO_2/CeO_2 catalysts. In terms of DRIFT analysis, they found that the addition of Ca significantly reduced the formation of NH on catalyst surface, which limited its reaction with NO to form N_2O. Furthermore, authors also proposed that Ca addition caused a deceased formation of NO_2, reducing its reaction with NH_3 to form N_2O, further increasing the N_2 selectivity of the catalysts. Yang *et al.*[129] studied the relationships of N_2 selectivity of NO reduction over MnO_x-CeO_2 with the GHSV and the reactants' concentrations. They proposed that N_2O formation over MnO_x-CeO_2 mainly resulted from the E-R mechanism (*i.e.*, the reaction between over activated NH_3 and gaseous NO), and the L-H mechanism (*i.e.*, the reaction between adsorbed NH_3 species and adsorbed NO_x) did not contribute to N_2O formation.

5.2 CeO_2/TiO_2 system

The combination of ceria with titania can be reasonably assumed for NH_3-SCR due to the excellent redox property of ceria and good acidity of titania. In comparison with VO_x/TiO_2 catalyst, CeO_2/TiO_2 owns the merit of environment-benign. Moreover, much higher surface area can be obtained by ceria, suggesting that in addition to be used as surface dispersed component, ceria can also be used as support, leading to the novel configuration of TiO_2/CeO_2. Actually, in our recent work,[130] we reported the application of TiO_2/CeO_2 catalyst in NH_3-SCR and negligible differences in activity and selectivity were found between TiO_2/CeO_2 and CeO_2/TiO_2 catalysts in the absence of SO_2. This exactly accords with Zhang *et al.* Conclusion[81] that interfacial Ce-O-Ti are the active sites of Ce-Ti oxides in NH_3-SCR.

Both Lewis and Brønsted acid sites are found on CeO_2/TiO_2. Besides, various surface nitrate species (*i.e.*, bridging nitrates, bidentate nitrates, monodentate nitrates and free nitrate ions) are detected during the NO+O_2 adsorption. From an *in situ* DRIFTS investigation, our recent result[121] shows that surface nitrate species in CeO_2/TiO_2 can only be replaced by but not react with the adsorbed NH_3 species. On the other hand, NH_3 adsorbed on Lewis acid sites are considerably consumed after introduction of the NO+O_2 stream. As no NO_2 signal is observed, it is supposed that the reaction is mainly happened between adsorbed NH_3 on Lewis acid sites and gaseous NO.

In contrast to our result, NO_2 was observed by Li *et al.* in the stable and transient adsorption experiment of CeO_2/TiO_2.[131, 132] As well, combined with other characterizations, a temperature-dependent reaction mechanism was proposed by them. That is, below 200 °C, the coordinated NH_3 reacts with adsorbed NO_2 to form N_2 (L-H mechanism). When the reaction temperature is higher than 200 °C, coordinated NH_3 species reacts with gaseous NO to

form nitrite and nitrate which then decomposed to N_2 (E-R mechanism).

It should be noted that the modification of CeO_2/TiO_2 by other component may change its reaction pathway. Li *et al.*[131] reported that the addition of tungsten oxide to CeO_2/TiO_2 catalyst is beneficial for the SCR reaction, and the reaction mechanism transfers from L-H to E-R at low temperature range (< 200 °C). Shu *et al.*[107] conducted a study on the SCR of NO over Fe modified CeO_2/TiO_2 catalysts. They proposed coordinated NH_3 and ionic NH_4^+ species as well as adsorbed NO_2 might be the key intermediates in the reaction. Except for the reaction between NO_2 and ammonia, the reaction between ammonia and nitrate species was unlike to occur. In the relatively low-temperature range (<200 °C), the coordinated NH_3 and ionic NH_4^+ as well as in situ formed NO_2 species were considered to be involved in the NH_3-SCR reaction following an L-H mechanism. In the relatively high temperature range (>200 °C), Lewis acid Fe^{3+} species acted as active sites, where the reaction between gas-phase or weakly adsorbed NO and NH_2 species occurred following an E-R mechanism. For a $Ti_{0.9}Ce_{0.05}V_{0.05}O_{2-\delta}$ catalyst, Huang *et al.*[36] suggested that high active monodentate nitrate and bridging nitrate species as well as abundant ionic NH_4^+ (Brønsted acid sites) were the key intermediates in the low temperature SCR reaction.

5.3 WO₃/CeO₂ system

In NH_3-SCR reaction, WO_3 is famous for its usage as an additive for V_2O_5/TiO_2 catalysts to enhance the acid property and hinder the rutilization of TiO_2.[133] Taken into consideration of the poor acidity of ceria, the incorporation of WO_3 into ceria is highly desired.

It is important to note that after incorporation of MnO_x or TiO_2, the type of acid sites of ceria is not much changed, making the discrimination of the contribution of acid sites from different species difficult. In contrast, the distinct different signals from Lewis acid and Brønsted acid as obtained by ceria and WO_3 species offers the possibility to accurately explore the activity contributions from different acid sites. Moreover, the separate providing of acid sites and redox sites by WO_3 and CeO_2 implies synergistic interaction probably dominates the performance of WO_3/CeO_2 catalysts in NH_3-SCR.[76]

Chen *et al.*[134] found that the low-temperature activity of WO_3-CeO_2-TiO_2 catalysts was sensitive to the catalyst composition especially under low-O_2-content atmospheres. It is attributed to the synergistic effect between CeO_x and WO_x in the catalysts. On one hand, the interaction between ceria and tungsten oxide promotes the activation of gaseous oxygen to compensate the lattice oxygen consumed in NH_3-SCR (selective catalytic reduction) reaction at low temperatures. On the other hand, the Brønsted acid sites mainly arise from tungsten oxides, Lewis acid sites mainly arise from ceria. Both acid sites facilitate the adsorption of NH_3 on catalysts and improve the stability of the adsorbed ammonia species, which are beneficial to the NH_3-SCR reaction.

Ma *et al.*[69] conducted an investigation of WO_x modification effect on CeO_2 catalyst for NH_3-SCR. Polytungstate (WO_x) species were identified as the main species, and due to the interaction between CeO_2 and WO_x, the Brønsted acidity of catalysts remarkably increased but the amount of surface oxygen decreased. Based on

literature and their experimental results, they proposed two reaction routes for SCR over CeO_2 and WO_x/CeO_2 catalysts (Figure 5). For ceria, ammonia is mainly adsorbed on Lewis acid sites, and the active surface oxygen accelerates the successive H-abstraction process of NH_3 to form NH_2 and NH species. NH then reacts with NO and O_2 to form N_2O and the further oxidation of NO generates NO_2. The consumed surface oxygen can be rapidly supplemented by gaseous oxygen. For WO_x-containing catalysts, NH_3 adsorption is promoted. Meanwhile, the decreased amount of surface oxygen prevents the excessive de-protonation of NH_3 species to NH. More NH_2 species form from NH_3 deprotonated by bridging oxygen from W-O-Ce and W-O-W domains. NH_2 reacts with NO and O_2 to generate water and nitrogen. The decrease of surface oxygen inhibits the generation of NO_2 from NO. The oxygen vacancies left behind by the reaction of bridging oxygen are further oxidized by gaseous oxygen.
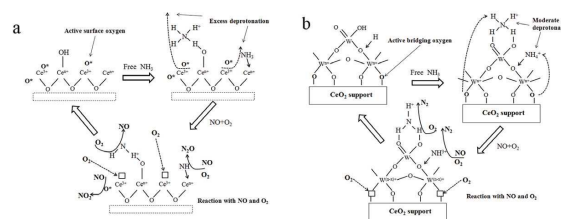

Fig. 5 Proposed models for the NH_3-SCR reaction route on (a) CeO_2 and (b) WO_3/CeO_2 catalysts.[69]

Recently, Li *et al.*[59] carried out a study by *in situ* Raman spectroscopy to identify the active sites on WO_3/CeO_2 catalyst for NH_3-SCR. Isopolytungsten species, $Ce_2(WO_4)_3$ and crystalline WO_3 were observed on ceria surface. After exposure of the catalyst to NH_3 at 200 °C, the signals corresponding to crystalline WO_3 and $Ce_2(WO_4)_3$ species were weakened, implying that NH_3 was selectively chemisorbed on the surface of WO_x. Importantly, simultaneously with the decreased intensity of W=O vibration, the Raman band at 858 cm^{-1} due to the W-O-W vibration in $[WO_4]$ or $[WO_6]$ units appeared and increased when NO and O_2 were introduced. It provides powerful evidence that either the $[WO_4]$ or $[WO_6]$ units are active during reaction between the adsorbed NH_x species and the gaseous NO_x species. In contrast, when the order of gas treatment was reversed, no discernible difference was observed between the Raman spectra. This suggests that the reaction between the adsorbed nitrate species and the NH_x species is very weak or cannot take place at 200 °C. Based on these results, a synergistic reaction mechanism consisting of two independent cycles was proposed by them. That is, NH_3 firstly interacts with surface $Ce_2(WO_4)_3$ and changes the W=O to W-O. The newly formed $[WO_4]$ or $[WO_6]$ units becomes a more active intermediate species through the neighboring oxygen atom bonded to cerium (owing to the good OSC and reducibility of CeO_2). Then the NH_x ($x < 3$) species react with NO or NO_2 to produce N_2 and H_2O, and the reduced Ce^{3+} cation can be returned to its original state, fulfilling the SCR cycle.

6. SO₂ and H₂O tolerance of ceria-based catalysts in low-temperature NH₃-SCR

In the real circumstance of NH_3-SCR, SO_2 and H_2O are always contained in the stream and their concentrations are dependent on the working conditions. It is commonly recognized that the presence of SO_2 and/or H_2O is adverse to the NH_3-SCR performance, and this effect is even more evident at lower temperatures. Thus, the SO_2 and H_2O tolerance of ceria-based catalysts in low-temperature NH_3-SCR constitutes one of the most important topics for its final application.

6.1 SO_2 tolerance of ceria-based catalysts

To gain insight into the SO_2 tolerance of ceria-based catalysts, the exploration of the interaction between SO_2 and ceria is essential. Ferrizz et al.[135] have studied the interaction of SO_2 with ceria thin-film using XPS and TPD techniques. They found that a small fraction of the adsorbed SO_2 was oxidized to SO_4^{2-} by ceria at room temperature. Accordingly, three SO_2 desorbed peaks attributed to molecularly adsorbed SO_2 and decomposition of adsorbed sulfates were observed at 200, 610 and 690 ^{o}C. Contrastively, Smirnov et al.[136] demonstrated by XPS results that sulfite ions were the main surface species when exposing of ceria to SO_2 at temperature lower than 200 ^{o}C, and sulfate ions were produced when the temperature was higher than 300 ^{o}C. In addition to chemical valence, the existence state of sulfur species is also studied in literature. Waqif et al.[137] revealed by IR spectroscopy results that SO_2 oxidation on ceria gave rise to two bands in 1340-1400 cm^{-1} and near 1200 cm^{-1}, which were associated with two main types of sulfates: surface and bulk-like species. They also pointed out that the relative amount of the two sulfates depended on the surface area and total sulfate amount formed. Nevertheless, the temperature-dependent feature of these species and their effect on the catalytic performance in NH_3-SCR are not mentioned. In our recent study,[138] the points have been addressed. It was found that the sulfation process was gradually deepened, and the existence states of sulfate species over CeO_2 were changed from surface sulfates to bulk-like sulfates and to bulk sulfates with raising the sulfated temperature. Meanwhile, the formed bulk-like and bulk sulfates were the main reason to result in the decrease of catalytic activity (Figure 6). Interestingly, it is found that the bulk sulfates can be removed by H_2O washing, providing an effective way to reduce the SO_2 poisoning of ceria-based catalysts.
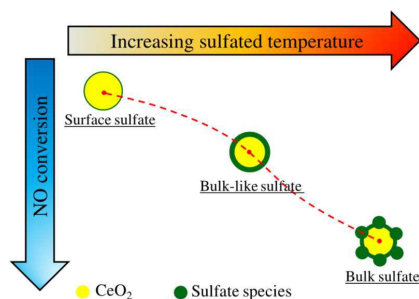
Fig. 6 Schematic view of relationships between the existence state of sulfate species and NO conversion over the sulfated CeO_2.[138]

From the above discussion, it is known that under mild conditions (e.g., relatively low temperatures), Brønsted sites can be introduced into pure ceria due to oxidation of SO_2 to sulfate ions, and this exhibits a promotional effect on the catalytic performance after SO_2

exposure.[54, 139] Moreover, by taking advantage of the strong interaction between SO_2 and ceria, the employment of ceria as an additive to the catalyst component can alleviate the sulfation of the main active phase, which improves the SO_2 tolerance of catalysts. For instance, Jin et al.[140] studied the role of cerium in the improved SO_2 tolerance for NO reduction with NH_3 over Mn-Ce/TiO_2 catalyst at low temperature. Their results indicated that after introduction of CeO_2, SO_x ad-species preferentially formed on ceria as bulk-like sulfate species and thus lessened the sulfation of the main active phase (MnO_x) (Figure 7). In addition, the DRIFT and TG-DSC results indicated that Ce modification could reduce thermal stabilities of the sulfate species covered on catalyst surface, thereby promoting its decomposition. Both of them contribute to the improved SO_2 tolerance of Ce modified catalysts. Similar result was also reported by Kwon et al. in V/Sb/Ce/Ti catalysts.[141]
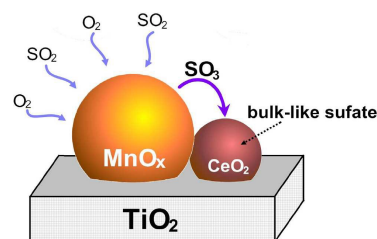
Fig. 7 Formation pathway of bulk-like sulfate on Mn-Ce/TiO_2 samples.[140]

Despite the obvious enhancement of NH_3-SCR activity for ceria-based catalysts in the present of SO_2, it is important to note that owing to the strong basic property of ceria, the gradual sulfation of ceria from catalyst surface to bulk seems to be inevitable, which incurs the ultimate poisoning of catalyst. He et al.[142] studied the deactivation of CeO_2/TiO_2 catalyst by SO_2 in NH_3-SCR. Conversion of NO remained above 90% in the presence of 100 ppm SO_2 at 350 °C for 48 h. However, when 180 ppm SO_2 was added at 300 °C, NO conversion only remained above 90% during the first 12 h and then gradually decreased with time. Characterizations of fresh and SO_2-poisoned CeO_2/TiO_2 catalysts implied that there was no obvious change in the crystal structure of the different samples; however, the specific area decreased with SO_2 poisoning time. Sulfates were formed and preferentially diffused from the surface to a bulk phase during the poisoning process. They proposed that the main reason for the deactivation was that SO_2 could react with the catalyst to form high thermally stable $Ce(SO_4)_2$ and $Ce_2(SO_4)_3$, resulting in the disruption of the redox properties between Ce(IV) and Ce(III) and the inhibition of the formation and adsorption of nitrate species.

From this aspect, the weakening of interaction between ceria and SO_2 seems to be key point to extend the SO_2 tolerance of ceria-based catalysts. In general, the combination of ceria with inert materials like SiO_2 and Al_2O_3 can not only increase the surface area and dispersion of the active component, but also the acidic property of the catalyst is improve, which neutralizes some of the basic sites in ceria and in turn weakens the interaction between SO_2 and ceria. As expected, this is advantageous to the final activity and SO_2 tolerance.[143]

Along this line, in our recent works, strategies to lessen the SO_2 poisoning of ceria-based catalysts are developed. By adoption of a novel TiO_2/CeO_2 configuration, it is found that the SO_2 tolerance is greatly improved when comparing with the normal CeO_2/TiO_2 and pure ceria samples.[130] This is mainly attributed to the coverage of ceria surface with a component (TiO_2) that has poor interaction with SO_2. In addition to provide Ti-O-Ce active sties, the surface covered TiO_2 can also play the role of protection layer that lower the bulk sulfation of ceria (Figure 8). Besides surface modification, we also find that the bulk doping of foreign ions in ceria is effective to improve the SO_2 tolerance. Metal ions doped (M = Ti^{4+}, Sn^{4+}) ceria was prepared and used as a support to fabricate MnO_x/CeO_2 catalysts.[102] These modified catalysts are found to exhibit improved catalytic activity and better resistance to sulfur-poisoning, and the Ti doped sample shows no activity lost after 10 h test at 250 ^{o}C.
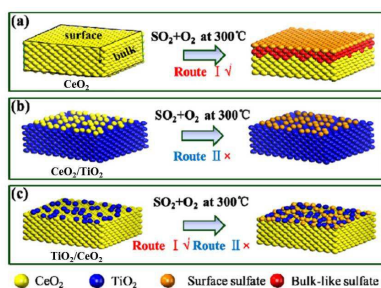

Fig. 8 Proposed reaction routes of NH_3-SCR over CeO_2, CeO_2/TiO_2 and TiO_2/CeO_2 in the presence of SO_2.[130]

Lastly, it is important to note that in addition to the sulfation of main active component, the deposition of NH_4HSO_4 on the surface of catalysts is another notable reason for the deactivation of catalysts at low temperatures. The decrease of decomposition temperature of NH_4HSO_4 is reported to be an effective strategy.[108] Nevertheless, the related researches are limited and much effort on this aspect is still needed.

6.2 H$_2$O tolerance of ceria-based catalysts

Owing to the competition adsorption of H_2O with NH_3, H_2O generally shows a reversible negative effect on NH_3-SCR, and this is particularly true for the reaction operated at temperature lower than 200 ^{o}C. In fact, water is one of the main components in the flue gas and a product of SCR reaction. It can interact strongly with the surface of the catalysts, possibly modifying the structure of the active sites and allowing the retention of high oxidation state. However, in comparison with SO_2 tolerance, the H_2O tolerance of catalysts in NH_3-SCR is much less studied.

Gao *et al.*[144] conducted experimental and theoretical studies on the influence of water vapor on the performance of a Ce-Cu-Ti (CCT) oxide catalyst. They found that H_2O inhibited the SCR performance of the CCT oxide catalyst at low temperatures, while it promoted SCR performance at temperatures above 300 ^{o}C. NH_3 adsorption profiles showed that the presence of H_2O greatly decreased the NH_3 adsorption amount, especially the weakly adsorbed NH_3 part, and DFT calculations showed that H_2O would compete with NH_3 to be adsorbed on the catalyst and inhibit NH_3 oxidation. The inhibition

effect of H_2O at low temperatures was attributed to the competing adsorption of H_2O with NH_3, while the promotional effect at high temperatures was due to the inhibition of NH_3 oxidation. Yang and co-workers[145] studied the influence of H_2O on the low-temperature NH_3-SCR reaction over MnO_x-CeO_2 catalysts. A novel promotion effect on the catalytic performance was observed due to the inhibition of N_2O formation by H_2O. It was proposed that the inhibition of N_2O formation over MnO_x-CeO_2 by H_2O was not only attributed to the competition adsorption of H_2O with NH_3 but also related to the decrease of the oxidation ability of MnO_x-CeO_2 in the presence of H_2O. Casapu *et al.*[146] explained this effect as a two-step process. H_2O firstly adsorbed and hydroxylated the surface of the catalyst. Then, N_2O and hydroxyl groups reacted with each other in a dehydration reaction leading to the formation of N_2.

By surveying the literature, it is found that up to now, almost all of the reported works on the increase of H_2O resistance is based on the improvement of activity of catalysts, such as increase the acid and redox properties. For example, Liu *et al.* reported that Mn-Ce mixed oxide catalyst prepared by surfactant-template method exhibited higher resistance against H_2O and SO_2 than that prepared by co-precipitation method. Charaterization results revealed that the surfactant-templated MnO_x-CeO_2 catalyst owned higher surface area, which contributed to the adsorption and activation of NH_3 as well as NO_x.[147] In consideration of the essential reason for H_2O deactivation, the decrease of H_2O affinity to the catalysts without disrupting the acidic and redox properties seems to be the key point to deal with the H_2O tolerance problem. In our recent study, we find that by modification of the pore structures of catalysts, the low-temperature NH_3-SCR in the presence of H_2O can be greatly enhanced.[148]

7. Conclusions and perspectives

Low-temperature SCR is a potential technique to reduce the serious NO_x emissions and meet the stringent environment regulations. Researchers in the field of academia and industry are making great efforts to develop low-temperature catalysts that can work well around 250 ^{o}C or even below. Among them, ceria-based catalysts have received considerable attention owing to their rich reserves, favorable textual property, good redox ability and high oxygen storage capacity. In addition to be used as a support or promoter, ceria can also act as the major active species in NH_3-SCR, which combines the functions of VO_x and TiO_2. The using of ceria can promote NO adsorption and accelerate NO oxidation to NO_2 or nitrites, thereby prompting the "fast SCR" reaction. Moreover, ceria can disperse and have strong interactions with other transition metal oxides, possibly changing the chemical and redox features of foreign species and generating new active sites.

It should be noted that although considerable progress has been achieved, challenges are still existed in the exploitation of highly active ceria-based catalysts for low-temperature NH_3-SCR. Till now, only MnO_x/CeO_2 can acquire complete NO conversion at lower temperatures (100-150 ^{o}C), and most of the reported ceria-based catalysts merely accomplish full conversion of NO at temperature of 200 ^{o}C or higher. Improvement of the low-temperature activity is no doubt helpful to fulfill the entire temperature requirement. To strengthen the performance of ceria-based catalysts in low-temperature NH_3-SCR, fully exploiting the potential of ceria is

needed. As we know, apart from chemical compositions, the performance of ceria-based catalysts is highly dependent on their structures. To achieve high activity, the catalysts with high surface area, special porous structures and controlled morphologies are required. With great progress being made in the synthesis of nanostructured ceria-based materials, fascinating new opportunities are present. Therefore, future studies should focus more on the fabrication of ceria-based catalysts with controlled structures and morphologies for enhanced performance.

Another big challenge for ceria-based catalysts in low-temperature NH_3-SCR is the durability. In comparison with the medium temperature operations, the competing adsorption of H_2O with NH_3 and the deposition of $(NH_4)_2SO_4/NH_4HSO_4$ on catalyst surface are more evident at low temperatures and this brings significant damage to the long term stability of catalysts. Additionally, even in the absence of SO_2 and water stream, the deposition of NH_4NO_3 on catalyst surface can be occurred when the reaction temperature is lower than the decomposition temperature of NH_4NO_3, and this will also cause serious problems since the deposited NH_4NO_3 can lead to the reduction of surface area and coverage of the active sites.[33] All these tremendously affect the practical use of ceria-based catalysts in low-temperature NH_3-SCR. Unfortunately, investigations on these aspects are relatively neglected, and substantial efforts are required in the future studies.

Acknowledgements

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Graphical Abstract
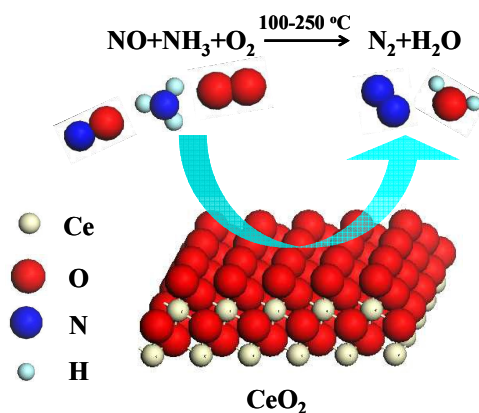
$$NO+NH_3+O_2 \xrightarrow{100\text{-}250\ ^\circ C} N_2+H_2O$$

- Ce
- O
- N
- H

CeO$_2$

Low-temperature NH$_3$-SCR has attracted considerable attention owing to the vast demand in industrial furnaces and feature of energy-conserving. This review summarizes the recent advances in the application of ceria-based catalysts for low-temperature NH$_3$-SCR.