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NO direct decomposition: Progresses, challenges and opportunities

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NO direct decomposition is deemed as the ideal technology to diminish NO from exhaust waste owing to its cost-effectiveness and eco-friendliness characteristics. However, its wide application is seriously impeded by the low activity and stability of catalysts under the real conditions. Here, the advances of catalysts for NO direct decomposition have been reviewed including noble metals, simple metal oxides, rare-earth oxides, complex metal oxides and zeolites, focusing on their distinctive properties and trying to provide the thoughts on the catalyst development over more than one century. The present knowledge of the active sites and various catalytic mechanisms for NO direct decomposition is also introduced. Afterwards, the challenges facing the catalysts with respect to the susceptibility in various co-fed gases are discussed in detail. Finally, candid suggestion on the opportunities to achieve the practical application of NO direct decomposition technology is put forward. It is expected that more efforts can be put into it and thus accelerate the development and application of this ideal NO removal technology.

1 Introduction

Nitrogen oxides, usually in the exhaust gases of fixed sources and mobile sources, seriously hamper the environment and human health in the form of acid rain, photochemical smog and greenhouse effect.^[1] Priority needs to be given to NO because most nitrogen oxides (> 95%) is NO. Various techniques have been proposed to remove NO:^[2,3] for fixed sources, selective catalytic reduction (SCR) has been widely used in the industrial and general power plants. For mobile sources, three-way catalysts (TWCs) have already been commercialized to purify exhaust gases from gasoline-engine vehicles. Among those technologies, NO direct decomposition ($\text{NO} \rightarrow \frac{1}{2} \text{N}_2 + \frac{1}{2} \text{O}_2$) stands out as the ideal technology owing to the eco-friendly products and no requirement of reductants such as NH_3 , urea or hydrocarbons^[4,5] since it was proposed in 1906.^[6]

Although the decomposition of NO is thermodynamically feasible ($\Delta G = -86.6 \text{ kJ mol}^{-1}$ @ 100 °C), it is kinetically demanding owing to the strong binding energy between N and O ($\sim 630.6 \text{ kJ mol}^{-1}$) and thus high activation energy ($\sim 335 \text{ kJ mol}^{-1}$).^[4,5] Accordingly, the core of this technology lies in the catalyst. Over more than one century, various materials have been proposed to catalyze the NO direct decomposition (Fig.

1): noble metals,^[6,7] simple metal oxides,^[8-11] rare-earth metal oxides (REOs),^[12,13] complex metal oxides,^[14-22] zeolites,^[23,24] and other catalysts.^[25,26] However, the activity of the catalysts is still far from requirement. Table 1 lists composition of representative exhaust gases.^[27] It infers that an excellent catalyst for NO direct decomposition needs to be highly active, e.g., the conversion of NO to N_2 is higher than 90% at moderate temperatures (300-850 °C) with the coexistence of various gases at high space velocity. However, most of the catalysts show poor resistance to O_2 , which is a serious obstacle for their wide application. Furthermore, the catalysts are susceptible to CO_2 , H_2O and SO_2 poisoning. A lot of challenges have to be addressed before the application of NO direct decomposition.

Accordingly, instead of detailed introduction of NO direct decomposition itself and exhaustive description of all kinds of catalysts,^[4,5,28-30] this review summarizes the efforts in developing catalysts for NO direct decomposition, trying to provide the thoughts on the catalyst development over the years. The present knowledge of the active sites and catalytic mechanisms in the NO direct decomposition community is also introduced. Afterwards, the challenges within the technology in terms of the susceptibility in various co-fed gases are discussed in detail. Finally, the opportunities to handle the challenges by density functional theory (DFT) calculation, single-atom catalysis, surrounded-type catalysts, aqueous electrochemical methods, and operando characterization are proposed. We hope that more efforts can be put into it and thus accelerate the development and application of this ideal technology for NO abatement.

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Fig. 1 Development timeline of catalysts for NO direct decomposition over more than one century, from noble metals,^{6,7} simple metal oxides,^{8–11} rare-earth oxides,^{12,13} complex metal oxides^{14–22} to zeolites^{23,24} and other catalysts.^{25,26} The values are the N₂ yields of the catalysts at corresponding temperatures unless otherwise specified.

Table 1 Composition of exhaust gases from mobile and stationary sources.^[27]

Source	T (°C)	[Nitrogen oxides] (%)	[O ₂] (%)	Other (%)
Diesel engines	200–400	0.002–0.07	5–10	CO _x (10), H ₂ O (10), HC (0.05–0.1), SO _x (0.01–0.05), particulates
Power plants	400–450	0.04–0.1	4–10	CO _x (5–7), H ₂ O (10–15), SO _x (0.001–0.3)

2 Advances in catalyst development for NO direct decomposition

2.1 Noble metals

The noble metals are the first studied catalysts for NO decomposition. In 1906, Jellinek^[6] found that Pt wire showed a relatively high activity. Green and Hinshelwood^[31] later reported that 13.5% NO was decomposed in 57 s at 1450 °C. The specific activity of noble metals decreased in the order of Pt ≈ Pd > Rh > Ru.^[32] DFT calculation results showed that the activity of stepped sites at the metal surfaces decreased in the order of Pd > Pt > Rh > Ru > Ag > Au.^[33]

To reduce the cost and slow down the sintering process, supported noble metal catalysts were developed.^[9,34–36] The NO conversion to N₂ was ~70% for 9%Pd/γ-Al₂O₃ at 900 °C and 1.6 g s cm⁻³; appropriate alloying with Au and Ag can further enhance the activity and durability in O₂ and SO₂.^[37] The support has a significant effect on the activity. Pd supported on MgAl₂O₄, achieved the NO conversion to N₂ of 73% at 750 °C, 0.75 g s cm⁻³ and maintained at 23% in the presence of 2.5% O₂.^[7] More than 90% NO was decomposed at 700 °C over 20 wt% Pd/SiO₂ and Pd/BeO catalysts; the turnover frequency (TOF) decreased as Pd particle size decreased for Pd/SiO₂ whilst increased for Pd/BeO.^[38] The termetallic catalyst of Pt-Ir-Au/Al₂O₃ (atomic ratio Pt:Ir:Ru = 8:1:1) exhibited 40% NO conversion and 100% N₂ selectivity at 700 °C and 0.8 g s cm⁻³.^[39]

Although the noble metals have relatively high catalytic activity, the high reaction temperature impeded their practical application. To alleviate this issue, Luo *et al.*^[40] loaded 1 wt% Rh on carbon nanotubes (CNTs), which achieved 100% NO conversion at only 450 °C and 0.06 g s cm⁻³. However, the high

activity might be attributed to the reduction effect of CNTs rather than the Rh catalyst itself. The zeolite support can

effectively reduce the reaction temperature.^[41–45] Pd and/or Cu loaded mordenite catalysts achieved 100% NO conversion at 400 °C with the selectivity order of CuMOR > PdCuMOR-I > PdCuMOR-II > PdMOR.^[42] The selectivity to N₂ was promoted when Mo and Pd were incorporated into MOR (Mo_{0.3}Pd_{1.9}MOR) at 400 °C.^[45] Since the metal ion-exchanged zeolite itself has decent activity at moderate temperatures especially Cu ion-exchanged zeolite catalysts as discussed later, it seems that the activity enhancement of noble metals by zeolite support is limited.

2.2 Simple metal oxides

To reduce the cost, simple metal oxides were developed as catalysts for NO direct decomposition.^[8,9,35,46] Winter systematically studied the catalytic properties of 40 metal oxides at 330–870 °C. The activation energy (*E_a*) varied in the range of 37.7–171.6 kJ mol⁻¹.^[47] The TOF values of CuO, NiO, Fe₂O₃ and Al₂O₃ were 6.6 × 10⁻⁴, 2.2 × 10⁻⁵, 1.5 × 10⁻⁵ and 5.5 × 10⁻⁶ s⁻¹ at 700 °C, whereas Co₃O₄ and ZrO₂ were 1.9 × 10⁻² s⁻¹ at 600 °C and 3.5 × 10⁻⁴ s⁻¹ at 900 °C, respectively.^[35] The results indicated that Co₃O₄ was one of the most active catalysts among the simple metal oxides. Later results^[11] showed that the pure Co₃O₄ was actually inactive, the high activity previously reported was originated from the residual alkaline elements from the precipitation agents such as Na₂CO₃ during preparation (Fig. 2a). The presence of Na facilitated the desorption of oxygen from Co³⁺ to form Co²⁺ via the formation and decomposition of NaNO₃, and Co²⁺ was the active site for NO decomposition. Such results were proved by further studies. As shown in Fig. 2b, the activity of Co₃O₄ can be remarkably enhanced by loading alkaline or alkaline-earth metal ions,^[48,49] and Ba was the most effective loading species. The activity decreased at temperatures higher than 627 °C due

to the thermal reduction of Co_3O_4 to CoO , which is of low activity.

Fig. 2 Catalytic activity of (a) Co_3O_4 prepared using different precipitation agents and (b) Co_3O_4 loaded with different alkali metals with atomic ratio M/Co of 0.035 for NO decomposition. Reaction conditions: NO = 1000 ppm, gas flow rate = $30 \text{ cm}^3 \text{ min}^{-1}$, W/F = 0.5 g s cm^{-3} . Reprinted with permission from ref. 48. Copyright (2003) Elsevier B.V.

The alkaline/alkaline-earth metal ions have been proved effective to promote the activity of many simple metal oxides besides Co_3O_4 . The parent Ce and Mn mixed oxides (CeMn) showed very limited activity. The addition of 5 wt% Ba (5 wt% Ba/CeMn) increased the N_2 yield to 68% at 800 °C and 1 g s cm^{-3} , even higher than that of 3 wt% Pd/ Al_2O_3 (65.5%).^[50] Besides, K impregnated Co-Mn-Al mixed oxides showed decent long-term stability at 612 °C and gas hourly space velocity (GHSV) of $61 \text{ g}^{-1} \text{ h}^{-1}$, maintaining ~20% NO conversion for over 200 h.^[51] Alkali/alkaline earth metals played multiple roles including increasing the surface area, creating basic sites to promote the NO adsorption, facilitating the desorption of O_2 and forming active sites, leading to enhanced activity. It should be noted that pure Ba or BaO itself is almost inactive towards NO decomposition,^[52] but Ba supported on MgO showed high activity.^[10,53]

2.3 Rare-earth metal oxides

Similar with the alkaline-/alkaline earth-metal loaded Co_3O_4 , the REOs, especially those with the C-type cubic structure, display high activity to catalyze NO decomposition but at higher temperatures (Fig. 3).^[12,54–61]

Tsujimoto *et al.*^[62] systematically investigated the activity of REOs and found that the activity was strongly dependent on the crystal structure. Since the coordination environment of the rare earth ions strongly determines the extent of NO adsorption, lower coordination numbers (CN) facilitate greater adsorption of NO on the surface of REOs. The C-type cubic structure is a double-edge fluorite structure with one-fourth of the oxygen sites vacant and regularly ordered (Fig. 4a). Its lattice volume is larger than that of A- and B-type structure and thus it has larger cavity space, which is beneficial for NO decomposition. Accordingly, the C-type cubic REOs (CN = 6) showed higher activity than the A- (CN = 7), B- (CN = 7 and 6), and fluorite-type (CN = 8) oxides (Fig. 4b). For the C-type series, the basicity is the most important factor. The activity

increased with the density of surface basic sites (Fig. 4c). Eu, Gd, and Dy oxides showed relatively high activity.

Since both oxide ion vacancy and basicity are important for

Fig. 3 Catalytic activity of various REOs as a function of temperature. Consult the related references for the specific reaction conditions with slight differences.^{12,54–61}

REOs, controlling them can modify the activity. Co-substitution of the Gd-sites with Ba and Y introduced oxide ion vacancy and lattice strain, which promoted the NO direct decomposition. At $> 750 \text{ °C}$, the $(\text{Gd}_{0.70}\text{Y}_{0.26}\text{Ba}_{0.04})_2\text{O}_{2.96}$ catalyst was the most active among $(\text{Gd}_{1-x-y}\text{Y}_x\text{Ba}_y)_2\text{O}_{3-y}$, with 100% NO conversion and 60% N_2 yield at 750 °C and 3 g s cm^{-3} . Furthermore, it exhibited decent oxygen-resistance, with N_2 yield of 22% at the presence of 10% O_2 .^[12] There was a balance between accelerated oxygen desorption and increased number/strength of basic sites, thus the doping amount had an optimal value.^[57] Among the C-type cubic REOs, $(\text{Y}_{0.69}\text{Tb}_{0.30}\text{Ba}_{0.01})_2\text{O}_{2.99+5}$ displayed the highest activity, with 100% NO conversion to N_2 at 900 °C and 3 g s cm^{-3} , which was ascribed to the accelerated oxygen desorption via the redox cycle of $\text{Tb}^{3+}/\text{Tb}^{4+}$ and increased basic sites and content of oxide ion vacancy by Ba doping.^[13] The

activities of REOs can be considerably increased by Ba impregnation. The catalytic activity of Ba-impregnated REOs at 900 °C and 1 g s cm⁻³ decreased in the order of Ba-Dy₂O₃ ≈ Ba-Sm₂O₃ ≈ Ba-Y₂O₃ > Ba-Nd₂O₃ > Na-Tb₄O₇ > Ba-La₂O₃ >> Ba-Pr₆O₁₁. Ba-Dy₂O₃ showed the highest NO conversion to N₂ (57%) in the absence

Fig. 4 (a) Representative A-type, B-type, and C-type R₂O₃ (R: rare earths) structures. (b) Effect of the rare earth elements on the catalytic activity of the REOs. (c) Dependencies of the activity of REOs on the density of the basic sites. Reprinted with permission from ref. 62. Copyright (2015) Wiley-VCH.

of O₂.^[63] Highly dispersed Ba species facilitated the formation, adsorption, stabilization and subsequent reaction of NO₂, thus higher activity.

Besides those C-type cubic REOs, Pr₆O₁₁ with cubic fluorite-type structure was also active to catalyze the NO direct decomposition, 52% N₂ yield at 900 °C, 3 g s cm⁻³ and further to 69% with the addition of Mg and Ca ((Pr_{0.86}Mg_{0.07}Ca_{0.07})₆O_{11-δ}).^[59] The Mg and Ca doping introduced oxide ion vacancies, making the structure close to the C-type cubic structure and thus higher activity. Moreover, Ce_{0.8}Mn_{0.15}Ba_{0.05}O_x catalyzed 77% NO decomposing to N₂ at 800 °C and 1 g s cm⁻³ although pure CeO₂ was almost inactive.^[54] Introduction of Mn led to the generation of oxide ion vacancies, which was beneficial for the catalytic activity. The recent work by Reddy *et al.*^[64]

revealed that in the CeO₂-M_xO_y binary metal oxides prepared by the co-precipitation method, CeO₂-Co₃O₄ and CeO₂-NiO catalysts exhibited higher activity and N₂ selectivity compared to CeO₂-Fe₂O₃ and CeO₂-CuO. Surface characterization showed that both Co and Ni resulted in the presence of Ce³⁺/Ce⁴⁺ and M²⁺/M³⁺ (M = Co, Ni). The synergy between these dual redox sites was the origin of higher activity. Remarkably, the Ce-Ni catalysts exhibited 100% N₂ selectivity at 400 °C and >95% selectivity at 450-650 °C (GHSV = 2100 h⁻¹). Such results are encouraging, which shed lights on the development of high-performance catalysts in the intermediate temperatures.

2.4 Complex metal oxides

The complex metal oxides such as perovskite-type (ABO₃) and perovskite-like (A₂BO₄) oxides (Fig. 5a) subsequently emerged for their appealing activity at elevated temperatures on NO direct decomposition (Fig. 5b),^[16,17,65-70] thermal stability and sulfur-poisoning resistance at temperatures > 500 °C, and composition versatility with strong elemental accommodation at both A- and B-sites.^[28,71] Dating back to 1979, Shin *et al.*^[14] proposed the importance of disordered oxide ion vacancies to NO decomposition catalysis based on their study on Sr₂Fe₂O₅ and Ca₂Fe₂O₅ with disordered and ordered oxide ion vacancies, respectively. They further investigated the adsorption of NO on SrFeO₃ and speculated that the NO molecules adsorbed on Fe³⁺ with some oxide ion vacancies and the Fe³⁺/Fe⁴⁺ redox couple helped the formation of NO⁻ species.^[72] Subsequently, various kinds of perovskites were studied to catalyze the NO decomposition.

The lanthanum-based perovskites attract much attention. The NO conversion to N₂ decreased in the order of LaNiO₃ > LaCoO₃ > LaMnO₃ > LaFeO₃ > LaCrO₃, correlating with the amount and temperature of O₂ desorption.^[73] Nevertheless, LaNiO₃ showed only 24% NO conversion to N₂ at 700 °C and 3 g s cm⁻³. In order to improve the activity of LaCoO₃ and LaMnO₃, La_{0.8}Sr_{0.2}CoO₃ and La_{0.4}Sr_{0.6}Mn_{0.8}Ni_{0.2}O₃ were prepared by doping Sr at the A-site and Ni at the B-site.^[15] The N₂ yield increased to 55 and 66% at 800 °C and 1 g s cm⁻³, respectively, due to the introduced oxide ion vacancies.^[74] Likewise, the activity of LaMnO₃ can be improved by doping at the La- and Mn-sites. The activity enhancement increased in

Fig. 5 (a) Schematic structure of ABO₃ and A₂BO₄ type perovskite oxides, (b) catalytic activity of various perovskite-type and perovskite-related oxides. Consult the related references for the specific reaction conditions with slight differences.^[16,17,65–70]

the order of Ba > Sr > Ca for the La-site due to the introduction of oxide ion vacancy, whilst In > Ga for the Mn-site due to the weakening of B–O bond and thus easier desorption of O₂.^[17] Particularly, La_{0.7}Ba_{0.3}Mn_{0.8}In_{0.2}O₃ displayed the highest N₂ yield (64%) at 800 °C and 3 g s cm⁻³ among those catalysts.^[17]

The barium-based perovskites show promising activity towards NO direct decomposition. The activity of BaMnO₃ was significantly promoted through doping and increased in the order of La > Pr for the Ba-site whilst Mg > Zr > Fe > Ni > Sn > Ta for the Mn-site. Ba_{0.8}La_{0.2}Mn_{0.8}Mg_{0.2}O₃ catalyst showed the highest yield of N₂ (74%) at 850 °C and 3 g s cm⁻³.^[70] NO direct decomposition over strontium-based perovskites such as SrMnO₃ and SrFeO₃ was also investigated.^[66,70]

Similar to the case of ABO₃ oxides, the activity of A₂BO₄ is closely associated with the content of oxide ion vacancy. LaSrNiO₄ showed NO conversion of 95% at 900 °C and 1.34 g s cm⁻³, much higher than La_{0.1}Sr_{0.9}NiO₃ (58%) and LaNiO₃ (29%), with La₂NiO₄ being the lowest (18%), in agreement with the trend of oxide ion vacancy content.^[16] On the other hand, the N₂ selectivity followed the order of LaSrNiO₄ > La₂NiO₄ > LaSrNiO₃ > LaNiO₃, demonstrating the higher selectivity of A₂BO₄-type oxides towards NO decomposition. According to Zhao *et al.*,^[16] the oxide ion vacancies and lower valent ion (Ni²⁺) are the active centers; the catalysis proceeds via a redox mechanism. Further modification with Ce or Mn at the La- or Ni- sites enhanced the activity, i.e., La_{0.5}Ce_{0.5}SrNiO₄ and LaSrMn_{0.2}Ni_{0.8}O_{4+δ} showed 54% and 83% N₂ yield at 800 °C (W/F = 2.4 g s cm⁻³) and 850 °C (W/F = 1.2 g s cm⁻³), respectively.^[65,75] Small amount of thorium doping at the La-site of La₂CuO₄ increased the activity by 6% at 500 °C and GHSV of 7500 h⁻¹. Attractively, La_{1.867}Th_{0.100}CuO₄ reduced at 300 °C achieved significantly high NO conversion to N₂ (~91%) at 650 °C, which were attributed to the cation defects, oxide ion vacancies and Cu⁺ ions in the reduced samples.^[68]

Another complex metal oxide is Ba₃Y₄O₉-based perovskite-related material, which showed relatively high activity at high temperatures and a large NO storage capacity at low temperatures due to the large content of intrinsic oxide ion

vacancies.^[19] Partial substitution of Y with Sc can further increase the activity due to the accelerated oxygen desorption, but the activity is not high enough and the stability is insufficient.^[76] The very recent results showed that the 10% Cu-doped material, Ba₃Y_{3.6}Cu_{0.4}O₉, displayed the N₂ yield of 81% at 700 °C and 3 g s cm⁻³ and good stability under 1% O₂ co-feeding conditions.^[21]

One problem with the complex metal oxides is the low surface area due to the high calcination temperature generally used. To address this issue, various methods have been proposed.^[71] Our work showed that loading BaCoO₃ onto CeO₂ can significantly increase the surface area, from 7.3 m² g⁻¹ for BaCoO₃ to 35.9 m² g⁻¹ for 5%BaCoO₃-CeO₂. Accordingly, the N₂ yield increased from 27.2% to 70.1% at 750 °C and 1.5 g s cm⁻³ although the electronic factor also played an important role.^[22] The La₂CuO₄ nanofibers, prepared by the hydrothermal method, showed 100% NO conversion to N₂ and O₂ at ≥ 300 °C and 60,000 h⁻¹. In contrast, the La₂CuO₄ bulk powder showed only 78% conversion at 800 °C.^[18] Furthermore, the nanofiber catalysts showed high NO conversion and stability (~96%) whereas the bulk powder catalysts exhibited dramatically decreased activity (from 78 to 18%) over 60 h stream testing at 800 °C. Such appealing catalytic performance was attributed to the special nanofiber structure, which rendered significantly higher surface area (105 vs. 2.7 m² g⁻¹), appropriate ratio of Cu⁺/Cu²⁺ and free of adsorption competition between NO and O₂. Although high content of Cu⁺ is beneficial for the activity of La₂CuO₄ nanofibers, the activity of doped La_{2-x}A_xCuO₄ powder increased sharply with the increase in the average oxidation number of Cu.^[21] Accordingly, the influence of Cu⁺ and Cu²⁺ on the activity of La₂CuO₄-based materials needs further investigation.

2.5 Zeolites

Inspired by the high activity of Cu-exchanged Y-type zeolites (Cu^{II}/Y) for the reduction of NO with NH₃, Kagawa *et al.*^[23] investigated their performance during NO direct decomposition in 1978 and found that the catalytic activity

increased with the exchange level of Cu^{2+} ions. The Cu^{II}Y-69 (the number is the exchange level) showed 28% NO conversion and 16% N_2 yield at 500 °C and 1.3 g s cm^{-3} . However, the activity decreased with reaction time at 300–400 °C due to poisoning by the formed O_2 during the reaction, although it can be recovered after heating at 500 °C. Later, the Kagawa group^[24] found that Cu^{2+} -exchanged ZSM-5 zeolites showed very high and stable catalytic activity. The NO conversion and N_2 yield were 94 and 49%, respectively, at 550 °C and 1.0 g s cm^{-3} . Furthermore, the activity maintained stable at 500 °C for at least 30 h. Copper ions in the zeolite exist as Cu^+ and Cu^{2+} and undergo reversible redox reactions. Cu^+ ions produced at high temperatures act as the active sites; $\text{NO}^{\delta-}$ and $(\text{NO})_2$ adsorbed on Cu^+ are the active intermediates in NO decomposition.^[77] Generally, the highest activity is found at 500–550 °C, higher temperature results in decreased catalytic activity. It is not due to the deactivation of the catalysts; instead, it is probably due to the change of the reaction mechanism and/or the rate-determining step. Since then, lots of efforts have been paid to zeolites and found that the exchange level, zeolite structure and Si/Al ratio, and cocations have significant impact on the activity.^[24,78–87]

With the increase of Cu loading, the five-coordinated Cu^{2+} species transformed into four-coordinated square planar.^[88] A pair of Cu^{2+} lost a doubly charged oxide ion upon heating therefore forming Cu^+ , which was regarded as the active sites.^[83] Accordingly, excess loading of Cu^{2+} is an effective way to develop active catalysts for NO direct decomposition.

Iwamoto *et al.*^[81] investigated the influence of zeolite structure and $\text{SiO}_2/\text{Al}_2\text{O}_3$ (Si/Al) ratio on the catalytic activity of five different zeolites for NO direct decomposition. The content of Cu^{2+} available for NO adsorption was dependent on the zeolite structure. The Cu^{2+} -exchanged ZSM-5 (Z) zeolite with Si/Al of 23.3 showed much higher activity (67% NO conversion at ~520 °C and 1 g s cm^{-3}) than mordenite (M), ferrierite (F) and L-type (L) zeolites (Fig. 6a). In addition, the catalytic activity per cupric ion was proportional to the Si/Al ratio (Fig. 6b).

Fig. 6 (a, b) Influence of zeolite structure and Si/Al ratio on the NO direct decomposition activity. The activity in (a) and (b) was measured at 1.0 g s cm^{-3} and $P_{\text{NO}} = 2.1\%$. Reprinted with permission from ref. 81. Copyright (1989) Elsevier Science. (c) Influence of cocation loading and Cu exchange level on the NO direct decomposition activity. Reprinted with permission from ref. 90. Copyright (2000) Elsevier Science.

Iwamoto *et al.*^[79] observed the cocation effect on Cu-Y zeolite. Co^{3+} or Ni^{2+} exchanged Y zeolite showed no catalytic activity for NO direct decomposition whereas they improved the activity of Cu-Y. The N_2 yield increased from 6.4% to 7.1 and 8.4%, respectively, at 500 °C and 4 g s cm^{-3} . It suggested that the Co^{3+} or Ni^{2+} ions occupied preferentially inner inert sites whereas more Cu^{2+} ions would locate on the active super cage-sites. Similar results were found on the La- and Ni- co-doped Cu-ZSM-5.^[89] Yokomichi *et al.*^[90] systematically studied the influence of cocations on the catalytic activity of Cu-ZSM-5 for NO direct decomposition (Fig. 6c). Both theoretical calculation and experimental results show that the addition of Ca or Ni on Cu-ZSM-5 increased the activity by promoting the desorption of oxygen and maintained NO adsorption on the catalyst under the coexistence of H_2O . Many investigators reported the beneficial effect of REs. RECu-ZSM-5 (RE = La, Sm or Ce) showed much improved activity and hydrothermal stability during NO decomposition compared to the bare Cu-ZSM-5, by promoting the dispersion of Cu thus increasing Cu reducible sites.^[91] Yahiro *et al.*^[92] reported that only Sm and Gd were capable of stabilizing Cu^+ in Cu-ZSM-5 as the active sites among the RE ions (La, Ce, Pr, Nd, Sm and Gd). Those discrepancies are probably originated from the different preparation methods and testing conditions. Nevertheless, the cocation effect can be employed to improve the activity of zeolites.

2.6 Other catalysts

Fig. 7 (a, b) Catalytic activity of doped graphene. Reprinted with permission from ref. 26. Copyright (2018) American Chemical Society. (c) Catalytic activity of g-C₃N₄. Reprinted with permission from ref. 25. Copyright (2010) The Royal Society of Chemistry.

Besides those catalysts as discussed above, there are other catalysts emerging in recent years. Co₃AlO (CAO) and Co_{1.5}Ca_{1.5}AlO (CCAO) complex oxide catalysts derived from hydrotalcite-like compounds show decent activity.^[93] The N, S, and B-doped graphene was fabricated by thermally treating graphene oxide with heteroatom-containing precursors (Fig. 7a) and its catalytic activity was evaluated.^[26] The activity followed the order of N-doped graphene (NG) > S-doped graphene (SG) > B-doped graphene (BG) (Fig. 7b). The electronegativity, surface area, and functional groups played crucial roles. Especially, the pyridinic N and thiophene S can transfer extra electrons into π -antibonding of NO and thus weakening the N-O bond, leading to high activity. However, pure carbon (including graphene) exhibited limited activity and can be oxidized into CO or CO₂, carbon is preferred to be the reductant instead of catalyst. The activity of carbon in NO direct decomposition needs to be further clarified.

Graphitic carbon nitride (g-C₃N₄) was proved effective in catalyzing NO decomposition.^[25] The calculation results indicated that the oxygen of NO adsorbed on the nitrogen of C₃N₄, which is a Lewis basic site. The electron density can shift from the basic nitrogen site of the catalyst to the adsorbed NO and thus decreasing the bond order of N-O (Fig. 7c). The NO conversion of g-C₃N₄ was ~15% at 500 °C and 0.24 g s cm⁻³, which can be dramatically improved by loading Zn and Au to 69.4% and 41.0%, respectively. The side reaction of C₃N₄ + 6NO = 3CO₂ + 5N₂ happened although it was very limited. Stabilizing g-C₃N₄ for usage at high temperature is needed in future work.

3 Active sites and catalytic mechanisms

In order to design high performance catalysts for NO direct decomposition on purpose rather than “trial and error”, the insights into the catalytic mechanism are of great importance. To reach the mechanism, the knowledge of active sites on different types of catalysts and kinetic studies in the NO

decomposition community will be introduced briefly. The various catalysis mechanisms over different types of catalysts will be discussed in detail.

3.1 Active sites

Different kinds of catalysts possess different active sites. There are no consensus on the active sites even for the same type of catalysts. For the noble metal-based catalysts, NO might adsorb and then decompose only on the steps but not the terrace sites of Pd surface.^[94] Not only the noble metals themselves can serve as the active sites,^[95,96] but also the interaction with the support can help form active sites such as Pd species and Mg²⁺ ions.^[97]

For the metal oxide catalysts, the R₂-center (two adjacent F-centers of anion vacancies with a trapped electron),^[47] oxide ion vacancies,^[98] and basic sites^[48,49,99] have been proposed as the active sites. For REOs, the oxide ion vacancies are widely accepted as the active sites for NO adsorption and intermediate formation.^[13,21,76,100] For the ABO₃- and A₂BO₄-type oxides, both the B-site cation and oxide ion vacancy are the active sites.^[16,101,102] However, only a couple of vicinal oxide ion vacancies on the surface of ABO₃ are possible active sites; the redox recycle of metal ions at the B-sites (B = Co, Mn, and Ni) facilitated the electron transfer.^[74] The iron ion along with some oxide ion vacancies were the sites for NO sorption and forming nitrosyl ion species in SrFeO_{3-x} according to Shin *et al.*^[72] Cu⁺ was supposed to be the active center in La₂CuO₄ owing to the strong correlation between the activity and the average valence of Cu²⁺/Cu⁺ content in La₂CuO₄-based catalysts.^[103] The doping of metal with variant valences might lead to new active centers. Ce³⁺-(O)-(Ni²⁺-[]-Ni³⁺) might form on La_{1-x}Ce_xSrNiO₄, leading to much improved activity even under the coexistence of excessive oxygen.^[75]

Cu⁺ ions are widely recognized as the active sites on Cu-ZSM-5 zeolites,^[77,84,104,105] although Cu²⁺ also got few recognition.^[106] In addition, the reduced copper dimers ([Cu⁺-Cu⁺]) were reported to be the adsorption sites for NO.^[107] However, Sayle *et al.*^[108] claimed that both isolated copper and Cu-OH-Cu were the active sites.

3.2 Catalytic mechanisms

Various mechanisms have been proposed to explain the catalytic pathways for NO decomposition over different catalysts. The widely accepted points are that NO molecules adsorb on the active sites and are dissociated to form N₂ and O₂; the active sites are regenerated after the desorption of the produced N₂ and O₂ molecules. Nevertheless, it still remains controversial about the adsorption sequences of two NO molecules, the reaction intermediates, and rate determining step (RDS).

The Langmuir-Hinshelwood (L-H) model indicated that two NO molecules simultaneously adsorbed on the same active

Scheme 1 (a) Rideal-Eley (R-E) model. Reprinted with permission from ref. 47. Copyright (1971) Elsevier Inc. (b) proposed mechanism of NO decomposition over perovskite-type oxides. Reprinted with permission from ref. 74. Copyright (1998) The Royal Society of Chemistry. (c) Reaction mechanism of NO direct decomposition over Cu-ZSM-5 catalyst. Reprinted with permission from ref. 83. Copyright (1991) Elsevier B.V. (d) The “recycle” mechanism of NO decomposition over perovskite(-like) oxides. Reprinted with permission from ref. 111. Copyright (2005) Elsevier B.V.

Table 2 Rate equations of different catalysts for NO direct decomposition.

Catalyst	Elementary step	Rate equation	Ref.
Pt-Ni/Al ₂ O ₃ ^a	NO+* → NO* ^b	(1)	[34]
	2NO* → N ₂ +2O* (RDS)	(2)	
	2O* → O ₂ +2*	(3)	
		$r = \frac{kS^c K_{NO}^2 L_{NO}^2 P_{NO}^2}{(1 + K_{NO} P_{NO} + \sqrt{K_{O_2} P_{O_2}})^2} \quad [1] \quad \left(r = \frac{A^c P_{NO}^2}{(1 + B^c \sqrt{P_{O_2}})^2} \right)^f \quad [2]$	
Metal oxides and supported Pt ^a	NO+* → NO* (RDS)	(1)	[109]
	Os ^g +O* ↔ O ₂ +*	(2)	
Heated platinum wire	NO+* $\xrightleftharpoons[k_{-1}]{k_1}$ NO*	(1)	[95]
	NO+NO* $\xrightarrow{k_2}$ N ₂ O+O*	(2)	
	Os+O* $\xrightleftharpoons[k_{-3}]{k_3}$ O ₂ +*	(3)	
		$r = \frac{k_1 P_{NO}}{1 + K_1 P_{O_2} + K_2 P_{NO}} \quad (\text{H-L kinetics}) \quad [4]$	
		$r = \frac{k_2 P_{NO}^2}{1 + K_1 P_{O_2} + K_2 P_{NO}} \quad (\text{E-R kinetics}) \quad [5]$	
Mn ₂ O ₃ and Mn ₃ O ₄	NO+* $\xrightleftharpoons{K_{NO}}$ NO*	(1)	[98]
	2NO* $\xrightarrow{k}$ N ₂ +2O* (RDS)	(2)	
	or { 2NO* → N ₂ O*+O* N ₂ O* → N ₂ +O* }	(2)	
		$r = \frac{LkK_{NO}^2 P_{NO}^2}{(1 + K_{NO} P_{NO} + K_{O_2}^{1/2} P_{O_2}^{1/2})^2}$	
Ba/MgO, La ₂ O ₃ , Sr/La ₂ O ₃	2O* $\xrightleftharpoons{1/K_{O_2}}$ O ₂ +2*	(3)	[53,100]
	NO+* ↔ NO*	(1)	
	NO+NO* $\xrightarrow{k_2}$ N ₂ O ₂ * (RDS)	(2)	
	N ₂ O ₂ *+* → N ₂ O*+O*	(3)	
	N ₂ O* → N ₂ +O*	(4)	
		$r = \frac{N^k k_2 K_{NO}^2 P_{NO}^2}{1 + K_{NO} P_{NO} + K_{O_2}^{1/2} P_{O_2}^{1/2}} \quad [7]$	
		2O* ↔ O ₂ +2* (5)	

Alkali metal-doped cobalt oxide catalysts	$\text{NO}^* \leftrightarrow \text{NO}^*$	(1)	$r = \frac{Nk_3K_{\text{NO}}^2P_{\text{NO}}^2}{(1 + K_{\text{NO}}P_{\text{NO}} + K_{\text{NO}}^{1/2}P_{\text{O}_2}^{1/2})^2}$	[8]	[99]		
	$\text{NO}^* + \text{O}^{2-} \rightarrow \text{NO}_2^* + [\]^{-1}$	(2)					
	$\text{NO}_2^* + \text{NO}^* + [\]^{-1} \xrightarrow{k_3} \text{N}_2\text{O}_x^* + \text{O}^{2-} + *$	(3)					
	$(x < 3, \text{RDS})$	(4)					
	$\text{N}_2\text{O}_x^* + (x-1)^* \rightarrow \text{N}_2 + x\text{O}^*$	(5)					
Co- and Mn-based perovskite-type oxides	Scheme 1b		$r = \frac{k_2K_1NP_{\text{NO}}^2}{1 + K_1P_{\text{NO}} + K_4P_{\text{O}_2}}$	[9]	$\left(r = \frac{k_2K_1NP_{\text{NO}}^2}{K_1P_{\text{NO}} + K_4P_{\text{O}_2}} \right)$	[10]	[74]
$\text{La}_{0.7}\text{Ba}_{0.3}\text{Mn}_{0.8}\text{In}_{0.2}\text{O}_3$	$2\text{NO} + 2^* \leftrightarrow 2\text{NO}^*$	(1)	$r = \frac{(k_2P_{\text{NO}}^2 - k_2^{-1}K_3^{-1}K_4^{-1}P_{\text{N}_2}P_{\text{O}_2})[S_0]^2}{(1 + K_1^{1/2}P_{\text{NO}} + K_4^{-1/2}P_{\text{O}_2}^{1/2} + K_3^{-1}K_4^{-1/2}P_{\text{N}_2}P_{\text{O}_2}^{1/2})^2}$	[11]	[12]	[17]	
	$2\text{NO}^* \rightarrow \text{N}_2\text{O}^* + \text{O}^* \text{ (RDS)}$	(2)					
	$\text{N}_2\text{O}^* \leftrightarrow \text{N}_2 + \text{O}^* \text{ (fast step)}$	(3)					
	$2\text{O}^* \leftrightarrow \text{O}_2 + 2^*$	(4)					
Cu-ZSM-5	$^* + \text{NO} \leftrightarrow \text{NO}^*$	(1)	$r = \frac{k_{\text{app}}^n[\text{NO}]^2}{1 + K_{\alpha}^o[\text{O}_2]^{1/2}}$	[13]	[107]		
	$\text{NO}^* + \text{NO} \leftrightarrow (\text{NO})_2^*$	(2)					
	$(\text{NO})_2^* \rightarrow \text{O}^* + \text{N}_2\text{O}$	(3)					
	$^* + \text{N}_2\text{O} \leftrightarrow \text{N}_2\text{O}^*$	(4)					
	$\text{N}_2\text{O}^* \rightarrow \text{O}^* + \text{N}_2$	(5)					
	$\text{O}^* + \text{NO} \leftrightarrow \text{NO}_2^*$	(6)	$r = \frac{k_{\text{app}}[\text{NO}]^2}{1 + K_{\alpha}[\text{O}_2]^{1/2} + K_{\beta}^o[\text{NO}][\text{O}_2]}$	[14]			
	$\text{NO}_2^* \leftrightarrow ^* + \text{NO}_2$	(7)					
	$\text{O}^* + \text{NO}_2 \leftrightarrow \text{NO}_3^*$	(8)					
	$\text{NO}_3^* \leftrightarrow \text{O}_2^* + \text{NO}$	(9)					
	$\text{O}_2^* \leftrightarrow \text{O}_2 + ^*$	(10)					

^a Rate equations are obtained under the elimination of external diffusion. ^b * represents an active sites, X* represents the species adsorbed on the active site, eg., NO* represents adsorbed NO. ^c S represents number of adsorption sites quidistant from a given site. ^d L represents the total concentration of active sites. ^e A and B are constants. ^f Those rate equations in the parentheses are simplified under certain conditions. ^g Os represents surface mobile oxygen. ^h k and K represent the reaction rate constant and adsorption equilibrium constant, respectively. ⁱ [NO] and [O₂] represent the molar concentrations of NO and O₂. ^j α represents the conversion factor. ^k N represents the total number of active sites. ^l [] represents an oxide anion vacancy. ^m [S₀] represents the total number of adsorption sites. ⁿ k_{app} represents the apparent constant. ^o K_a = (K₆K₇K₈K₉K₁₀)^{-1/2} K_B = (K₃⁻¹K₄⁻¹)^{-1/2}

site,^[100] whilst the Rideal-Eley (R-E) model^[53] supported the successive adsorption and the reaction between the firstly adsorbed NO species and NO molecule colliding from the gas phase.^[95] Winter^[47] proposed similar catalytic mechanism as R-E over metallic oxides: the first NO molecule adsorbed on R₂-center; the second NO molecule subsequently attacked the F-center; the two adjacent NO adsorbed species reacted and released N₂; the R₂-center finally regenerated after the formation and desorption of O₂ (Scheme 1a). L-H mechanism was also used to explain the catalytic process of NO decomposition over Mn₂O₃ or Mn₃O₄,^[98] where two NO molecules adsorbed on the active sites simultaneously.

Besides the L-H and R-E models, Teraoka *et al.*^[74] proposed the reaction mechanism of NO direct decomposition over Co- and Mn-based perovskite-type oxides based on their study on the reaction orders of NO and O₂ in NO decomposition (Scheme 1b). In this mechanism, a pair of adjacent oxygen vacancies in the vicinity of the surface served as the active sites, on which the NO molecules absorbed successively. NO was adsorbed along with the oxygen atom that fit into the vacancy and an electron flowed to the NO molecule from the B-site cation neighboring the vacancy, giving rise to the formation of the NO⁻ species and the concomitant oxidation of

the B-site cation. Once the second NO molecule was adsorbed, a free N₂ molecule was released. The release of oxygen was regulated by the adsorption-desorption equilibrium of oxygen. The desorption of O₂ and recovering of the active center were accompanied by the redox change of B-sites ions. For Co- and Mn-based perovskite, the adsorption of the second NO molecule was the RDS. This mechanism has been widely accepted although with slight modification, such as the formation of N₂O^[17,53,100,110] or NO₂^[111] intermediate. It should be noted that N₂O or NO₂ can be possible by-product during the NO decomposition process either by NO_{ads} + N_{ads} → N₂O^[96] or 2NO + O₂ → NO₂ in the cool zone after the reaction system.^[17,100]

Generally, the nitrosyl (NO⁻) intermediate formed with NO molecule binding to the active center and accepting an electron.^[13,16,72,74] Iwamoto *et al.*^[83] reported a reaction recycle with Cu⁺ and NO⁻ as the active sites and intermediate species for the Cu-based zeolite catalysts (Scheme 1c), in which NO molecules adsorbed on the Cu⁺ sites to form Cu²⁺-NO⁻ species. Other species such as nitrite (NO₂⁻)^[53,63,99] and/or nitrate (NO₃⁻)^[21,48] were also supposed to be the intermediates based on the diffuse infrared Fourier transform spectrum (DRIFTS) results. According to Schay *et al.*,^[105] N₂ and O₂

molecules were decomposed from $\text{Cu}^{2+}(\text{O})(\text{NO})(\text{NO}_2)$ intermediates over the Cu-ZSM-5 catalyst.

Based on the O_2 -temperature programmed desorption (O_2 -TPD) and activity results of $\text{La}_{0.4}\text{Sr}_{0.6}\text{Mn}_{0.8}\text{Ni}_{0.2}\text{O}_3$, Zhu *et al.*^[111] proposed a “recycle” mechanism for NO direct decomposition over perovskite(-like) oxides (Scheme 1d). For this mechanism, NO was first adsorbed and dissociated into N_2 and atomic oxygen, which then reacted with another NO to form the adsorbed NO_2 . Afterwards, the adsorbed NO_2 desorbed and dissociated into NO and O_2 . In this process, NO_2 acted as an intermediate of O_2 formation. Xie *et al.*^[10] also reported that NO dissociated through a Ba- NO_2 species to generate N_2 and O_2 on the surface of Ba/MgO catalyst.

3.3 Kinetic studies

In order to figure out the reaction pathways, many kinetic studies were proceeded on NO decomposition catalysis by exploring the reaction orders and rate equations. The reaction orders ranged from 0.96 to 1.80 for NO, whilst -0.12 to -0.53 for O_2 , indicating the positive and negative effect of NO and O_2 , respectively.^[17,52,66,70,74,98,99] The indexes in the equations (Table 2)^[17,34,53,74,95,98-100,107,109] are consistent with the experimental results.

4 Challenges

4.1 O_2 -resistance

Poor oxygen resistance is a serious concern for NO direct decomposition catalysts. O_2 is either contained in the exhaust gases (1-15%) or produced from NO decomposition. Iwamoto and Hamada^[84] summarized the activities of different catalysts in the absence and presence of O_2 at 300-800 °C. 0.5% noble metal-loaded Al_2O_3 and perovskite-type oxides were almost completely deactivated with 5% O_2 feeding, whilst Co_3O_4 and

Cu-ZSM-5 zeolite showed moderate resistance to O_2 . Introduction of 0.5% O_2 decreased the maximum N_2 formation rate of Ba/MgO from 0.24 to 0.15 $\mu\text{mol g}^{-1} \text{s}^{-1}$ due to the transformation of the nitro intermediate to the nitrate species.^[10] Although the $\text{La}_{0.5}\text{-Ce}_{0.5}\text{-Si-Ni-O/MgO}$ exhibited decent N_2 yield of ~76% at 800 °C and 4 g s cm^{-3} , it decreased to 51% and then to 40% in the presence of 1 and 4% O_2 .^[112] Even worse, $\text{La}_{1.6}\text{Ba}_{0.4}\text{NiO}_{4-20\%}\text{BaO}$ lost ~55% N_2 yield at 850 °C and 1.2 g s cm^{-3} with the coexistence of only 0.6% O_2 .^[102] REOs showed appealing oxygen resistance, especially the Y_2O_3 -based materials. As shown in Fig. 8a,^[12,17,22,55-58,60,61,63,74,113] all the catalysts were sensitive to O_2 when its partial pressure was below 2%, whilst gradually became stable when it was beyond 2%. The inhibition of oxygen is reversible and the catalytic activity recovers to the original level.^[55,57,102,109,114] The oxygen resistance depends on the temperature due to easier desorption of oxygen species from the catalysts surface at higher temperatures (usually > 600 °C).^[17,114]

There were reports on the positive effect of O_2 on the activity. The activity of $\text{Ag/La}_{0.6}\text{Ce}_{0.4}\text{CoO}_3$ was pretty low in the absence of O_2 at 400 °C and 30,000 h^{-1} , with only ~5% NO conversion to N_2 . It soared up to 50% with 2% O_2 feeding, further to ~70% with the addition of 8% O_2 and eventually kept steady even in the presence of 20% O_2 .^[69] $\text{Ba}_2\text{YCu}_3\text{O}_{7-8}$ ^[115] and Fe-Mn/H-beta^[116] showed similar conversion tendency with O_2 concentration. It should be noted that all those results are not NO direct decomposition; instead, an intermediate NO_2 is probably formed by the reaction of NO and O_2 ; or the NO adsorption of the donor type ($\text{NO} \rightarrow \text{NO}^+$) is favoured when the catalyst surface is maintained in a highly oxidized state in the presence of O_2 .^[117]

In terms of the origin of O_2 inhibition, many investigators^[17,66,70,74,98] agreed that the competitive adsorption

Fig. 8 Effect of (a) O_2 , (b) CO_2 on the activity of NO direct decomposition. Consult the related references for the specific reaction conditions with slight differences^{12,17,22,55-58,60,61,63,74,113} in (a),^{13,27,50,58,60-62,116,127,128} in (b).

of oxygen on the surface of catalysts decreased their activity towards NO decomposition. Teraoka *et al.*^[74] suggested that the competitive adsorption of NO and O₂ on the active sites (a pair of adjacent oxide ion vacancies) made the regeneration of the active sites for subsequent catalytic cycles difficult. Haneda *et al.*^[99] proposed that the presence of O₂ led to the formation of the spectator species NO₃ instead of the active immediate species NO₂, which destroyed the active sites due to the strong adsorption, resulting in decreased catalytic activity.

Based on the discussion above, it is obvious that the oxygen desorption is difficult, which is mainly responsible for the poor oxygen resistance. Accordingly, lots of efforts have been devoted to enhancing the mobility and desorption of oxygen and thus to improve the oxygen resistance of the catalysts. The addition of Au and Ag decreased the temperature for oxygen desorption on Pd/Al₂O₃, which was regarded as the RDS for NO decomposition at < 750 °C, thus enhanced the catalytic activity in the presence of O₂.^[37] Cu doping into Ba₃Y₄O₉ can increase the content of surface oxide ion vacancies and the mobility of the lattice oxygen, which weakens the adsorption strength of oxygen and facilitates the recovery of the active sites.^[21] With the substitution of Ce, a new highly active site Ce³⁺-(O)-(Ni²⁺-[]-Ni³⁺) was formed, which promoted the mobility and desorption of oxygen and thus improved the activity and oxygen tolerance of La_{0.7}Ce_{0.3}SrNiO₄ at 850 °C.^[75] Our very recent results showed that the interaction of BaCoO₃ and CeO₂ prepared by the one-pot method remarkably increased the tolerance to O₂, with 54% NO conversion to N₂ at 800 °C and 1.5 g s cm⁻³ under 10% O₂ coexisting.^[22] According to the DFT results about the oxygen desorption on the cocation-loaded Cu/ZSM-5 catalyst, the introduction of Ca, Mg, Mn, Ni and Co ions lowered the desorption energy of O₂, shortened the bond distance and decreased the atomic charge of adsorbed oxygen on the catalyst, resulting in easier oxygen desorption.^[90]

The exposure to microwave has been proved to be very effective to remarkably enhance the catalytic activity and oxygen tolerance. The microwave exposed Fe(20%)/Na-ZSM-5 exhibited good endurance against oxygen with ~15% NO conversion decrease.^[118] Attractively, NO tended to decompose completely with ~100% selectivity to N₂ at the medium temperatures with excess O₂ feeding owing to the microwave catalytic effect, which has been found on different kinds of catalysts including BaMn_{1-x}MgO₃,^[20] MeO_x-Cu-ZSM-5 (Me = Mn, Ni),^[119] BaMeO₃ (Me = Mn, Co, Fe),^[120] Ba_{0.8}A_{0.2}MnO₃ (A = Ca, K, La)^[121] and MgCo₂O₄-BaCO₃^[122] (Fig. 9). Such outstanding resistance to O₂ is attributed to the microwave selective effect.^[20,123,124] Since the electromagnetic field is beneficial to activate polar molecules, the NO molecules adsorbed on the active sites can be activated by the microwave electromagnetic field but not O₂. Although both NO and O₂ can be adsorbed on the active sites, only NO molecules can be changed into chemical adsorption and further decomposed into N₂ and O₂. The O₂ molecules cannot be activated at such a low temperature because of the microwave selective effect.

NO decomposition is strongly inhibited by the produced oxygen, leading to low NO conversion. Accordingly, removal of oxygen in the system is effective to accelerate the NO decomposition.^[70] Based on that, the Caro group^[125] employed an oxygen separation membrane BaCo_xFe_yZr_{1-x-y}O_{3-δ} (BCFZ) hollow fiber membrane to remove the oxygen *in-situ* (Fig. 10). The adsorbed NO was catalytically decomposed on the surface of BCFZ membrane into N₂ and surface oxygen. The surface oxygen can be removed as oxide ions via the BCFZ membrane. Such a system achieved complete conversion of NO and ~95% N₂ yield even in the presence of 3% O₂ at 875 °C and 0.375 g s cm⁻³.^[125] Similar strategy was adopted by the Kawi group,^[126] where a BaBi_{0.05}Co_{0.8}Nb_{0.15}O_{3-δ} perovskite hollow fiber membrane was employed and achieved high NO removal

Fig. 9 (a) Comparison of oxygen inhibition on MCRM and CRM. Reprinted with permission from ref. 20. Copyright (2015) The Royal Society of Chemistry. (b) Effect of O₂ on N₂ yields of various catalysts towards NO direct decomposition under microwave irradiation.¹¹⁹⁻¹²²

Fig. 10 (a) Schematic diagram of NO decomposition with in situ removal of oxygen via perovskite membrane. Reprinted with permission from ref. 125. Copyright (2009) The Royal Society of Chemistry. (b) NO decomposition activity without and with O_2 removal using the $\text{BaCo}_{0.8}\text{Fe}_{0.2}\text{Zr}_{1-x-y}\text{O}_{3-\delta}$ hollow fiber membrane.¹²⁵

capacity at comparatively lower temperature (675–700 $^{\circ}\text{C}$) and high oxygen resistance. The results are encouraging. However, the complexity of the system makes its further exploration questionable.

4.2 CO_2 -resistance

CO_2 has similar negative effect on NO decomposition catalysis with O_2 (Fig. 8b).^[13,27,50,58,60–62,116,127,128] The negative effect of CO_2 was even stronger for catalysts including alkaline earth elements such as Ba, where CO_2 can strongly adsorb and thus hampered the activity. CO_2 tended to adsorb on the superficial oxygen species, thus reduced the adsorption sites for NO to form the intermediate species.^[27,69] The reaction order of CO_2 was -0.11 at 800 $^{\circ}\text{C}$ for 5 wt% Ba/CeMn catalyst, indicating the inhibitory effect of CO_2 . $\text{Ba}_{0.8}\text{La}_{0.2}\text{Mn}_{0.8}\text{Mg}_{0.2}\text{O}_3$ hardly endured the passive effect of CO_2 at 850 $^{\circ}\text{C}$ and 3 g s cm^{-3} ; the N_2 yield decreased from 70 to 30% when 1% CO_2 was introduced, then to only 18% for 5% CO_2 . It was due to the dissociative adsorption of CO_2 on the catalysts surface; the resulted CO strongly adsorbed at the active sites.^[128] For $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$, the N_2 yield was dramatically decreased from $\sim 58\%$ to only $\sim 10\%$ after introducing 5% CO_2 to 0.9% NO at 800 $^{\circ}\text{C}$ and 4 g s cm^{-3} , which was related with the formation of carbonate species.^[129] Nevertheless, the N_2 yield could completely restore to the original level without any destruction of the perovskite structure after excluding CO_2 .

In contrast, the C-type cubic REOs without alkaline metals show decent CO_2 endurance. $(\text{Yb}_{0.50}\text{Tb}_{0.50})_2\text{O}_{3\pm\delta}$ lost 20% NO conversion to N_2 at 900 $^{\circ}\text{C}$ and 3 g s cm^{-3} when 2% CO_2 coexisted in the feed gas, and then stayed stable conversion of 33% up to 5% CO_2 feeding.^[60] However, the inhibition became severer for the catalysts with alkaline earth metals such as Ba due to the strong tendency of acid CO_2 to adsorb on the basic sites of catalysts.^[61] The correlation between CO_2 deactivation degree and the number of basic sites on the catalyst over $(\text{Y}_{0.99-x}\text{Tb}_x\text{Ba}_{0.01})_2\text{O}_{2.99+\delta}$ ($x = 0, 0.1, 0.2, 0.3$, and 0.4), $(\text{Y}_{0.70}\text{Tb}_{0.30})_2\text{O}_{3+\delta}$, and Y_2O_3 catalysts revealed that it is the strong adsorption of CO_2 on Ba^{2+} sites that inhibited the activity.^[13] The zeolite-based catalysts are an exception, which

exhibited remarkable durability with CO_2 in the feed gas. The NO conversion over Fe-Mn/H-beta catalyst was almost unchanged as inlet CO_2 concentration increased up to 13% at 300, 350 and 400 $^{\circ}\text{C}$ ($\text{GHSV} = 20,000 \text{ h}^{-1}$),^[116] which is probably because the adsorption sites of NO and CO_2 on zeolite are different.^[130]

4.3 H_2O -resistance

The performance of catalysts in H_2O -containing atmospheres is an issue, but different for different catalysts. It has the dramatic impact on the zeolite-type catalysts. The catalytic activity of Cu-ZSM-5 and Cu-Y decreased with the addition of H_2O ,^[83,131] although it can be recovered by stopping the H_2O flow.^[86] The tolerance to water vapor at the elevated temperatures (high temperature hydrothermal stability) of zeolites is always a concern. The exposure to H_2O at high temperatures results in the destroy of the zeolite framework, dealumination, and migration/aggregation of Cu species and thus declined activity.^[132] H_2O can competitively adsorb on the same Cu^{2+} site as NO and formed $\text{Cu}(\text{OH})^+$,^[131] which reduced the amount of NO adsorption sites on Cu-MFI (from 4.35 to $0.22 \text{ cm}^3 \text{ g}^{-1}$).^[133] To enhance the endurance to H_2O , Ca and Ni were introduced into Cu/ZSM-5 to maintain the adsorption of NO in the presence of H_2O .^[90] Cu-ZSM-5 was almost inactive to the decomposition of NO under wet condition; however, RES-modified Cu-ZSM-5 still maintained partial activity.^[91] It inferred that the deactivation by H_2O was due to the transition of active copper species to inactive species such as CuO micro-clusters, which can be prevented by RE ions modification.

For the REOs and complex metal oxides, the inhibition effect of H_2O is much weaker^[55,69,134] and is dependent on the temperature. The Ag-loaded $\text{La}_{0.6}\text{Ce}_{0.4}\text{CoO}_3$ could keep moderate activity towards NO decomposition at 450 $^{\circ}\text{C}$ with the coexistence of 10% H_2O .^[69] The decrease of activity under wet steam was negligible and reversible for Cu-doped $\text{La}_{0.7}\text{Ba}_{0.3}\text{Mn}_{0.8}\text{In}_{0.2}\text{O}_3$.^[134] Promoted stability with the feeding of H_2O was achieved by microwave exposure,^[119–122,135] since the competitive adsorption between H_2O and NO on the same

active site was avoided to a large extent with the irradiation of microwave.

4.4 SO₂-resistance

SO₂ usually poisons the catalysts for NO direct decomposition, especially the ZSM-5 zeolite-based catalysts. SO₂ completely poisoned the activity of Cu-ZSM-5 at 400–650 °C. It tended to adsorb competitively with NO on the adsorption sites and prevented the catalytic reaction, although the activity can be recovered by desorption treatment at higher temperatures.^[86] 0.06% Ag-doped Pd/Al₂O₃ exhibited decent tolerance to SO₂ and thermal stability, holding 65% NO conversion to N₂ at 900 °C and 1.6 g s cm⁻³ with 540 ppm SO₂ feeding.^[37] 1% Ag modified La_{0.6}Ce_{0.4}CoO₃ also showed weaker inhibition by SO₂ than the unmodified sample.^[69] La_{0.7}Ba_{0.3}Mn_{0.6}In_{0.2}Cu_{0.2}O₃ experienced ~30% activity reduction after feeding 85 ppm SO₂ at 850 °C and 3 g s cm⁻³ during 3 h.^[134] The presence of SO₂ increased not only the amount of NO in the outlet steam, but also the time to reach a steady state for NO decomposition over CAO and CCAO catalysts. Moderate incorporation Ti into catalyst matrixes prohibited the adsorption of SO₂, thereby improved the durability with the feeding of SO₂.^[93]

4.5 Influence of coexistence of various gases

As aforementioned, practical composition of tail gas is very complex (Table 1).^[27] Accordingly, it is necessary to study the NO decomposition in the gas mixtures but such study is rather limited. La_{0.7}Ba_{0.3}Mn_{0.6}In_{0.2}Cu_{0.2}O₃ perovskite showed ~70% N₂ yield under 1% NO at 850 °C and 3 g s cm⁻³, which decreased to ~40% with the cofeeding of 1% O₂, 5% H₂O and 0.0085% SO₂.^[134] La_{0.87}Sr_{0.13}Mn_{0.2}Ni_{0.8}O₃₋₆ suffered ~10% reduction of NO conversion to N₂ when 1% O₂ and 1.6% H₂O were added to the feed (5% NO) at 650 °C and 6000 h⁻¹.^[27] Modification with 1% Ag was effective to improve the activity of La_{0.6}Ce_{0.4}CoO₃ from ~60 to ~70% at 450 °C and 30,000 h⁻¹ in 0.1% NO, 8% O₂, 10% H₂O and 0.01% SO₂.^[69] With the assistance of microwave irradiation, MgCo₂O₄–40%BaCO₃ achieved ~100% NO conversion and ~95% N₂ selectivity at 250–400 °C and 1 g s cm⁻³ in the mixture 0.1% NO, 5% H₂O and 5% O₂.^[122]

4.6 Influence of space velocity

Besides the various gases, the activity of catalysts for NO decomposition is still far from application especially under the actual working condition with high space velocity or low contact time.

The catalytic activity usually decreases with increased space velocity. The N₂ yield decreased from ~90 to ~35% when the space velocity was elevated from 0.15 to 7×10⁴ h⁻¹ for Ba₃Y_{3.4}Sc_{0.6}O₉.^[76] 1 wt% Pt/SrFe_{0.7}Mg_{0.3}O₃ lost ~40% activity when the space velocity increased from 0.15 to 4×10⁴ h⁻¹.^[66] Ba_{0.8}La_{0.2}Mn_{0.8}Mg_{0.2}O₃ exhibited ~75% N₂ yield towards NO decomposition at the space velocity of 0.18×10⁴ h⁻¹, whilst only ~20% at 4.5 × 10⁴ h⁻¹.^[70] La_{1.6}Ba_{0.4}NiO₄ also suffered serious reduction of N₂ yield by ~30% with increasing space velocity from 0.18 to 0.72×10⁴ h⁻¹.^[102] Similar phenomenon was found for Fe/NaZSM-5, over which NO conversion declined from 55 to 20% as space velocity changed from 0.18 to 1.08×10⁴ h⁻¹.^[118]

The low specific surface area of the catalysts should be partly responsible for the fast activity decrease with space velocity.

Briefly, O₂, CO₂, H₂O and SO₂ all impede the activity of catalysts towards NO decomposition individually or synergistically mainly by competitive adsorption with NO, although the inhibition effect is generally reversible. The negative effect is also observed as the contact time decreases or the space velocity increases. In sharp contrast, the presence of H₂ and HC is beneficial to achieve higher activity.^[27,36,40,117,125,128]

5 Opportunities and solutions

In order to realize the practical application of NO direct decomposition, multiple methods have been tried to promote the catalytic performance of catalysts. Besides the modification of various metal ions and the assistance of microwave as aforementioned, some extraordinary and promising strategies can be considered.

5.1 DFT calculation

Tajima *et al.*^[136] studied the NO direct decomposition over Cu-exchanged zeolite (ZCu) via Beck's three parameter hybrid DFT method with the Lee-Yang-Parr correlation function (B3LYP). The structure and energy of adsorbed species and intermediates with isolated Cu⁺, Cu⁰ or ZCu, respectively, were investigated. ZCu showed better activity due to the formation of $\pi(d-p)$ bond between ZCu and adsorbates. NO adsorption and dissociation as well as N₂ formation on Ir (100) surface were also calculated by the DFT method.^[137] It indicated that NO molecules adsorbed on Ir (100) surface following the order: bridge site > top site > hollow site. The adsorbed species tended to diffuse from the bridge or top sites to the hollow sites and then dissociate. N₂ was produced from the recombination of those adsorbed nitrogen atoms instead of the disproportionation reaction ($N + NO \rightarrow N_2 + O$). DFT results can also provide information of the adsorption and dissociation of NO, O₂ and N₂ on different facet (close-packed, stepped, kinked and open type), further revealing the structure dependence of NO direct decomposition.^[138] Accordingly, DFT calculation can shed light on the R&D of catalysts for NO direct decomposition and the catalytic reaction mechanisms.

5.2 Single-atom catalysts

In 2011, the Zhang group^[139] proposed the single-atom catalysts (SACs) for the first time, where the Pt single atom loaded on FeO_x showed excellent activity and stability towards CO catalysis oxidation. Since then, numerous studies focus on SACs in various fields.^[140] In terms of NO removal, Ding *et al.*^[141] used DFT to analyze the NO reduction by CO over single atom Pd embedded in CeO₂ (111) catalyst. It demonstrated that Pd₁/CeO₂ can achieve high selectivity to N₂. Pd₁-O_v served as the active site, on which two NO molecules absorbed to form the N₂O₂^{*} intermediate and then N₂ after two deoxygenation steps. Although there was no related

experimental report on single atom catalysis for NO direct decomposition, it is expected to be feasible considering the noble metal catalysts with moderate activity. However, new catalysis mechanism is probably involved^[142,143] and needs to be explored.

5.3 Surrounded catalysts

The issues related to catalysts sintering and poisoning by coexisted gases (O₂, CO₂, H₂O, SO₂, etc.) always impede the application of NO direct decomposition. To address that, the surrounded catalyst may be an alternative. Different from the traditional supported catalysts, the active components are surrounded by the supports in the surrounded-type catalysts, which can achieve better dispersity and higher interface area/density. The outer supporting materials usually possess excellent resistance to sintering and coexisting gases and thus protect the inner active sites from agglomeration and excessive adsorption of other gases except NO. Through regulating the ion-exchange degree and the compositions of metal hydroxide precursor and solution of support precursor, surrounded-type catalysts with different structures including the core-shell, inverse and gradient, etc. can be synthesized. Hao *et al.*^[144] synthesized the surrounded catalyst Ni@Al₂O₃ with core-shell structure through the ion-exchanged inverse loading method to catalyze the CO methanation reaction. Ni@Al₂O₃ reached 100% CO conversion ≥ 280 °C, 100 °C lower than that for the traditional impregnated Ni/Al₂O₃. Furthermore, it remained complete conversion of CO at 500 °C for at least 100 h. They also used the method to prepare the surrounded catalysts Ni@CeO₂ with inverse structure and Ni@Cu with gradient structure, which exhibited excellent activity and stability towards catalytic transfer hydrogenation and semihydrogenation of phenylacetylene, respectively. Upgrading the conventional supported-type catalysts to surrounded-type is expected to elevate the activity and stability for NO decomposition.

5.4 Application of aqueous electrochemical methods

The NO direct decomposition proceeds mainly through the redox reaction at elevated temperatures. Electrochemistry is a powerful technique to study the redox behavior. Thereby, it is rational to employ the aqueous electrochemical methods at room temperature to study the catalytic behavior at high temperatures,^[145] which can help screen excellent catalysts for NO direct decomposition. Actually, Zhu *et al.*^[146] used cyclic voltammetry (CV) in 1 mol L⁻¹ LiClO₄/PC (propanediol carbonate) electrolyte solution to study the redox performance of catalysts for NO direct decomposition. They suggested that the symmetry of the redox potentials in the CV curves represented the redox ability whereas the redox peak area is associated with the amount of active sites. The catalytic activity for NO reduction (with CO as the reductant) related to the redox peak area, whilst that for NO decomposition to the symmetry of redox potentials. Although there is some controversy over the reasonableness of this technique,^[147] it is worthy of further study.

5.5 Operando/*in-situ* characterization

One challenge with the design of high-performance catalysts lies in the catalytic mechanism. Although various mechanisms have been proposed, no consensus has been reached. The present catalysis mechanisms are mostly speculated from *ex-situ* characterization such as hydrogen-temperature programmed reduction (H₂-TPR) to reveal the reducibility of catalysts, NO/O₂-TPD to the sorption capability of NO and O₂, CO₂-TPD to the amount of basic sites. Nevertheless, proper operando/*in-situ* characterization is needed to explore the mechanism for NO decomposition.^[148,149] DRIFTS has been used to monitor the sorption behavior of NO and O₂ during NO decomposition,^[13,17,41,150,151] which can yield information regarding the intermediate species and thus help understand the reaction pathways. However, the sorption and reaction behavior of the co-fed gases such as CO₂, H₂O, or SO₂ still remain unclear. Electron spin resonance (ESR) probably can also provide information in terms of the sorption and/or reaction intermediates. The evolution of the crystalline structure during reaction, especially the oxidation states of cations and content of oxide ion vacancy, needs to be revealed. The X-ray adsorption spectra such as extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) are powerful techniques. In addition, The *in-situ* electron microscope can help observe the process of gas-solid reaction on the surface of nanoparticles, especially the phase and/or crystal structural evolution.^[152]

6 Conclusions

NO direct decomposition is the ideal denitration technology due to its simplicity and atomic economy. In this review, we comprehensively summarized the progresses of the catalyst development in terms of noble metals such as Pt and Pd, simple metal oxides such as alkaline/alkaline earth metal doped Co₃O₄, rare earth oxides such as C-type cubic oxides, complex metal oxides such as doped (La/Ba)(Co/Mn/Fe/Ni)O₃ and (La/Sr/Ba)₂(Ni/CuO)O₄, zeolite such as Cu-ZSM-5. Among those catalysts, noble metals, REOs, complex metal oxides need to work at higher temperatures (e.g., > 600 °C) to achieve acceptable activity. By contrary, simple metal oxides and zeolites can work at intermediate temperatures (400-650 °C). Although no consensuses have been reached on the active sites and catalytic mechanisms, the properties of oxide ion vacancy and basic sites generally determine the activity of oxide catalysts. Modifying the content of oxide ion vacancies and basic sites, and the basicity can improve the activity. However, the activity of the present NO direct decomposition catalysts is still not high enough to meet the demands of practical application, especially considering the tough conditions in the real world in terms of coexistence of various impure gases and high space velocity. Almost no exception, all the catalysts show poor resistance to O₂ either produced by NO decomposition or existed in the feed, which adsorb competitively with NO and reduce the active sites or make the regeneration of active sites difficult. Similar problems exist for

CO₂ via the dissociative adsorption and forming CO or via the formation of carbonate, especially for the alkaline earth metal such as Ba contained catalysts but it is needed for high activity. The co-existence of H₂O, SO₂ also has negative effect on the activity. Although in most cases, the activity can be recovered by stopping feeding those gases, it is a serious challenge for practical application especially considering the sharp decline of activity with increased space velocity.

Nevertheless, there is still light ahead. The microwave exposure has been proved effective to improve the activity and stability with the presence of various gases. The recent development in the catalysis fields such as DFT calculation, single atom catalysts, surrounded catalysts, which can help design and synthesize high-performance catalysts for NO direct decomposition. In addition, the room temperature aqueous electrochemistry probably can help screen catalysts for further application in NO decomposition. The greatest challenge lies in the mechanism. The operando/*in-situ* characterization of the catalysts along with computational work is believed to greatly advance our understanding of catalysis process during NO direct and thus help develop novel catalysts.

Conflicts of interest

There are no conflicts to declare.

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