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Review

Supported catalysts for simultaneous removal of SO₂, NO_x, and Hg⁰ from industrial exhaust gases: A reviewKe Zhao^a, Xin Sun^a, Chi Wang^b, Xin Song^a, Fei Wang^{a,*}, Kai Li^{a,*}, Ping Ning^a^a Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming 650500, China^b Faculty of Chemical Engineering, Kunming University of Science and Technology, Kunming 650500, China

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ABSTRACT

The simultaneous removal of SO₂, NO_x and Hg⁰ from industrial exhaust flue gas has drawn worldwide attention in recent years. A particularly attractive technique is selective catalytic reduction, which effectively removes SO₂, NO_x and Hg⁰ at low temperatures. This paper first reviews the simultaneous removal of SO₂, NO_x and Hg⁰ by unsupported and supported catalysts. It then describes and compares the research progress of various carriers, eg., carbon-based materials, metal oxides, silica, molecular sieves, metal-organic frameworks, and pillared interlayered clays, in the simultaneous removal of SO₂, NO_x and Hg⁰. The effects of flue-gas components (such as O₂, NH₃, HCl, H₂O, SO₂, NO and Hg⁰) on the removal of SO₂, NO_x, and Hg⁰ are discussed comprehensively and systematically. After summarizing the pollutant-removal mechanism, the review discusses future developments in the simultaneous removal of SO₂, NO_x and Hg⁰ by catalysts.

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1. Introduction

Pollutants, such as sulfur dioxide (SO₂), nitric oxides (NO_x), trace heavy metals and particulate matters (PMs) are typical components in industrial exhaust flue gas, which are harmful to both the environment and human health. SO₂ and NO_x are the main precursors of acid rain and toxic chemical smog [1,2]. Elemental mercury (Hg⁰) is among the most toxic heavy metals owing to high toxicity, volatility and bio-accumulation [3]. The flue gas contains three mercury species: Hg⁰, oxidized mercury (Hg²⁺), and particle bound mercury (Hg_p) [4]. Most of the Hg_p and Hg²⁺ can be effectively collected by conventional air-pollution control devices (APCDs) such as electrostatic precipitators, fabric filters and wet flue-gas desulfurization (WFGD) equipment, which are broadly installed in plants around the world [5]. However, Hg⁰ is relatively stable in the atmosphere, and (due to its chemical inertness, water insolubility, and volatility) is hardly removed by existing APCDs [6].

The current techniques for removing SO₂, NO_x and Hg⁰ are selective catalytic reduction (SCR) [7,8], WFGD [9], and activated-carbon injection [10,11]. However, individual pollutant-treatment systems are expensive to construct and operate, complex, prone to

instability, and require a high occupational area [12]. The current technologies for simultaneous removal of SO₂, NO_x and Hg⁰ include carbon-based material adsorption [13–15], photocatalytic oxidation [16,17], wet scrubbing [18–20], NH₃-SCR [7,8] and non-thermal plasma (NTP) technologies [21,22]. Carbon-based material adsorption and wet scrubbing have the disadvantages of secondary pollution and high investment costs. Photocatalytic oxidation and NTP have the disadvantage of limited industrial applications. Compared with these technologies, NH₃-SCR catalytic technology has the advantages of high efficiency, low energy consumption and low operating cost. This makes the catalytic method to remove SO₂, NO_x and Hg⁰ has become the main research direction for air pollution control. Initially, this research focused on SO₂, NO_x and Hg⁰ removal by catalysts without carriers, but the removal effect was non-ideal [23]. In later studies, the SO₂, NO_x and Hg⁰ removal was improved by loading active components (transition metals, rare metals, precious metals) on various carriers (carbon materials, metal oxides, metal-oxide frameworks (MOFs), zeolites) [24–28]. This review concludes the advantages and disadvantages of simultaneous removal methods, introduces the catalysts prepared by conventional and new carriers, and discusses the low-temperature performances of the catalysts. The mechanism of pollutant removal by catalysts is also discussed, as well as the possible research directions and future prospects.

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2. Removal technologies

Simultaneous removal technologies include carbon-based material adsorption [13–15], photocatalytic oxidation [16,17], wet scrubbing [18–20], NH_3 -SCR [7,8], and non-thermal plasma (NTP) technologies [21,22]. The removal techniques are summarized in Fig. 1. In carbon-based material adsorption, pollutants are often removed by modified activated carbon, active coke, or activated-carbon fibers, which have porous structures and strong adsorption capacities. However, carbon-based material adsorption is limited by high operating cost and quality degradation of fly ash [29]. Under UV/visible radiation, pollutants are oxidized by positively charged holes on the photocatalyst surface. A photocatalytic oxidation system can be worked at relatively low temperature and pressure [30], but the UV light source raises the energy consumption. In wet scrubbing technology, the oxidant solution in the scrubbing system (such as NaClO_2 , $\text{KMnO}_4/\text{NaOH}$ or H_2O_2) can oxidize NO and Hg^0 to soluble NO_2 and Hg^{2+} , which can then be removed by chemical solutions. However, this method produces large volumes of wastewater and high secondary pollution. NTP is a recently developed gas-phase oxidation method that removes multi-pollutants from flue gas [31,32]. NTP technologies remove pollutants quickly and efficiently, operating at atmosphere pressure and room temperature with no secondary pollution [33,34]. Their defects are high energy consumption and limited amount of flue gas; moreover, the high-voltage electricity poses a safety hazard that limits its industrial application [35]. Synergistic removal of NO and Hg^0 by existing NH_3 -SCR systems promises to overcome the disadvantages of previous simultaneous multi-pollutant-removal technologies. In the NH_3 -SCR system, NO is reduced to N_2 and H_2O by NH_3 , and Hg^0 is oxidized to Hg^{2+} by O_2 . The generated Hg^{2+} attaches to PM surfaces and is finally removed by electrostatic precipitators (ESP) or wet flue-gas desulfurization (WFGD) [36]. The NH_3 -SCR system improves the purification efficiency and lowers the operating costs of industrial exhaust flue-gas purification, without generating secondary pollution [12,37,38]. The present article systematically reviews the catalyst types, the key factors controlling the reaction processes, and the proposed reaction mechanisms of NH_3 -SCR technologies.

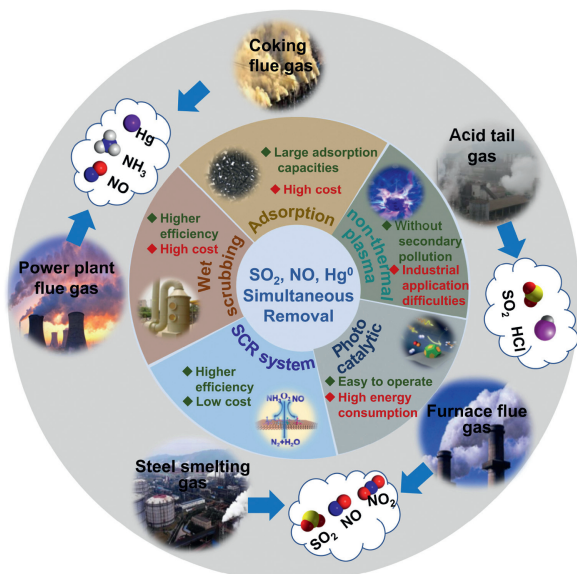


Fig. 1. Industrial exhaust gases source and simultaneous removal of SO_2 , NO and Hg^0 technology.

3. Simultaneous catalytic removal

The existing catalysts for simultaneous removal of NO and Hg^0 have been studied in the absence [23,39,40] and presence of carriers. Carriers can be divided into two main categories: conventional and new. Carbon-based materials [15,41–44], metal oxides [26,27,45–47] and silica [48,49] are among the conventional carriers, whereas molecular sieves [50–53], MOFs [28,54] and pillared interlayered clays (PILCs) [24,55] are new carriers. This paper reviews the differences between the conventional and new supported catalysts in the simultaneous removal of SO_2 , NO and Hg. Most supported metal-oxide catalysts are prepared by the impregnation method. In the presence of different carriers, the same active component can exhibit very different activities. However, as most catalysts are studied only in the laboratory, more research on their practical applications is needed.

3.1. Catalysts

3.1.1. Unsupported catalyst

Many catalysts used to remove NO_x , SO_2 and Hg^0 have been reported in the literature. Among the catalysts without carriers [23,39,40] are the CeO_2 - TiO_2 (CeTi) catalysts of Li *et al.* [39], which oxidize elemental mercury. They found that when the weight ratio of $\text{CeO}_2/\text{TiO}_2$ is 1:2, the CeTi catalyst exhibits higher Hg^0 oxidation activity in 150–250 °C, indicating that their superior performance was conferred by the high focuses of surface cerium and oxygen. Zhang *et al.* [23] researched TiO_2 - Al_2O_3 - CeO_2 materials synthesized by the sol-gel method, which simultaneously remove NO and Hg^0 . They found that $\text{TiAl}_{10}\text{Ce}_{20}$ nanoparticles supplemented by 10 wt% Al_2O_3 removed NO and Hg^0 with superior efficiency (93.41% and 80.54%, respectively) in an SCR atmosphere at 300 °C. Song *et al.* [56] studied the effect of Mn, Ti and Cu doping on simultaneous removal of NO and SO_2 of $\text{Fe}_{2.5}\text{M}_{0.5}\text{O}_4$ catalyst. The results show that the doping of the three metal oxides can significantly increase the removal rate of NO, but has no effect on the removal rate of SO_2 , because SO_2 can be completely removed under most conditions. Sun *et al.* [57] prepared a series of MFe_2O_4 ($\text{M} = \text{Mn, Zn, Cu, Ni, Co}$) catalysts to remove NO and SO_2 by hydrothermal method. They found that the removal rate of SO_2 at room temperature can reach 100%, and the CuFe_2O_4 catalyst has the highest activity compared to other catalysts. Shi *et al.* [58] studied the natural ferrous manganese ore to simultaneously remove NO, Hg^0 and toluene from flue gas. Activity evaluation experiments show that the maximum efficiencies of NO, Hg^0 oxidation are 95.29%, 83.0%. The characterization results show that the oxidation activity of manganese ore is mainly provided by Mn^{4+} and Fe^{3+} in it.

3.1.2. Catalysts based on conventional supports

Carbon-based catalysts: Carbon-based materials are the most commonly used adsorbents, which are often used to remove multi-air-pollutant from flue gas, including activated carbon, activated coke and activated carbon fiber [59–61]. Using an activated-carbon carrier, Song *et al.* [62] prepared 1%M-6%Y/AC (where M is Ni, Al or Mo) by equal-volume impregnation. The catalytic activity of simultaneous SO_2 and NO_x removal was maximized on the 1%Ni-6%Y/AC catalyst. Sumathi *et al.* [63] prepared a palm shell activated carbon (PSAC) adsorbent and loaded several metal oxides (Ni, V, Fe and Ce) on the ride to simultaneously remove SO_2 and NO_x . Among their sorbents, CeO_2/PSAC yielded the maximum sorption capacity for the simultaneous removal of SO_2 and NO_x . Sun [64] studied the catalytic activity of copper and iron-loaded microwave coconut shell activated carbon (MCSAC) with different loadings for simultaneous denitrification and mercury removal. The 15%Cu-5%Fe/MCSAC catalyst exhibited the best removal efficiency. The NO

removal rate was 86% and the mercury removal rate was 61% at 225 °C. In addition, effect of NH_3 concentration on removal of NO and Hg^0 was investigated, as shown in Fig. 2a.

Zhang *et al.* [65] studied the removal effect of $\text{FeCeO}_x/\text{CNTs}$ catalyst for NO and Hg and the SO_2 tolerance. They found that the NO and Hg removal rates of the catalyst were only 15.44% and 16.13%. Coating $\text{FeCeO}_x/\text{CNTs}$ catalyst with a layer of SiO_2 can significantly improve the activity and SO_2 tolerance of the catalyst. Li *et al.* [66] used activated coke as a medium to simultaneously remove SO_2 and NO_x from flue gas. It is found that AC still has high desulfurization and denitration efficiency after regeneration cycle. Zhao *et al.* [67] employed a $\text{CuO-MnO}_x/\text{AC-H}$ catalyst for the simultaneous removal of Hg^0 and NO from flue gas. They pointed out the significant role of the reaction temperature in physisorption and chemical oxidation. The optimal temperature for simultaneous removal of Hg^0 and NO_x was 200 °C. At this temperature, the 8% CuO -5% $\text{MnO}_x/\text{AC-H}$ catalyst achieved simultaneous removal efficiencies of 90% for mercury and 78% for NO_x . Zhu *et al.* [68] synthesized a series of $\text{V}_2\text{O}_5\text{-xCeO}_2/\text{AC}$ catalysts to investigate the capabilities of the catalysts to simultaneously remove Hg^0 and NO in the temperature range from 120 °C to 240 °C. They discovered through experiments that compared to 1 V/AC and 1 V-8Ce/AC, 8Ce/AC catalyst has the highest Hg^0 removal performance ($E_{\text{Hg}} > 98\%$) at 120–240 °C. The 1 V-8Ce/AC catalyst showed the best NO conversion performance compared to 1 V/AC and 8Ce/AC, 8Ce/AC, and the E_{NO} increased gradually from 55% to 86.9% with the increase of temperature (120–240 °C), as shown in Fig. 2b. Zhu *et al.* [44] used ammonium halide modified rice husk char to remove gaseous mercury. They found that the RHC adsorbent impregnated with ammonium bromide has excellent mercury removal performance, and can still reach an efficiency of about 80% for removing gaseous mercury. In addition, they found that this enhanced HgO removal adsorbent can

synergistically remove SO_2 and NO. Gao *et al.* [69] studied a series of $\text{CoO}_x\text{-CeO}_2$ loaded biomass activated carbon (CoCe/BAC) derived from maize straw. When removing both NO and Hg^0 at 230 °C, the 15% $\text{Co}_{0.4}\text{Ce}_{0.6}/\text{BAC}$ sample achieved 96.8% Hg^0 removal efficiency and 84.7% NO removal efficiency. Based on characterization analyses, the author attributed the best performance of 15% $\text{Co}_{0.4}\text{Ce}_{0.6}/\text{BAC}$ to its largest specific surface area, lowest crystallinity and strongest redox ability than other samples in the series. The NO removal was unaffected by low SO_2 concentration in the gas stream, and the NO conversion efficiency reached 80%, as shown in Fig. 2c.

Metal-oxide-based catalysts: Titania has stable physical and chemical properties, is non-toxic, and its surface area is below $100 \text{ m}^2/\text{g}$ [70]. TiO_2 has a certain acidity which enables it to be the main site of NH_3 adsorption in the $\text{NH}_3\text{-SCR}$ reaction and thus beneficial to the removal of NO_x . Therefore, TiO_2 is a common support widely used in $\text{NH}_3\text{-SCR}$ reaction. The most prevalent commercial catalyst is $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$, which delivers high activity but is active only within a narrow temperature window (300–400 °C) [71]. Zhao *et al.* [46] found that adding CeO_2 to the $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalyst can improve its catalytic activity for Hg^0 oxidation without using HCl. The co-catalyst CeO_2 shows satisfactory oxidation activity and improved water oxidation resistance. The promoted catalysts showed satisfactory oxidation activity and improved H_2O resistance. Wang *et al.* [72] studied the oxidation catalytic performance of VWTi catalysts with different loadings of CuO. The results show that the 7%Cu/VWTi exhibited high Hg^0 oxidation and a desired NO removal efficiency at 280–360 °C. Meng *et al.* [73] prepared a series of Mn-V-W/ TiO_2 (Mn-VWT) catalysts by impregnation to simultaneously remove Hg^0 and NO. The results show that Mn-VWT-400 has the best simultaneous removal performance. Its removal efficiency of Hg^0 and NO reached 100% and 82%, respectively. Yang *et al.* [74] used CeO_2 to modify $\text{V}_2\text{O}_5/\text{TiO}_2$ for simultaneous removal

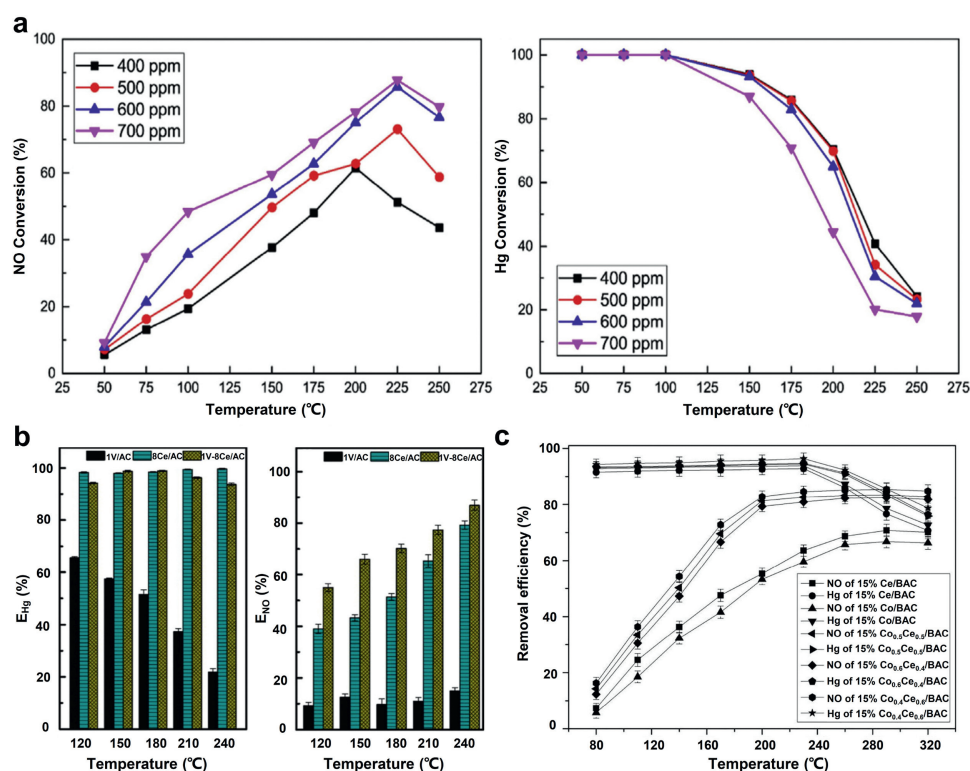


Fig. 2. (a) Effect of NH_3 concentration on removal of NO and Hg^0 for 15%Cu-5%Fe/MCSAC catalyst. Reproduced with permission [64]. Copyright 2019, Elsevier. (b) Simultaneous removal Hg^0 and NO over 1 V/AC, 8Ce/AC, and 1 V-8Ce/AC at different temperatures. Reproduced with permission [68]. Copyright 2019, American Chemical Society. (c) Effect of active ingredient on removal of NO and Hg^0 for 15% $\text{Co}_{0.4}\text{Ce}_{0.6}/\text{BAC}$. Reproduced with permission [69]. Copyright 2018, Elsevier.

of NO and Hg⁰. Experiments show that CeO₂ modification not only significantly improves the SCR performance, but also significantly enhances the oxidation of Hg⁰. Wang *et al.* [75] investigated the sulfated CuCl₂/TiO₂ catalyst to simultaneously remove NO and Hg. By characterizing the catalyst before and after vulcanization, it was found that the CuSO₄ generated on the catalyst increased the number of acid sites on the catalyst surface, thereby improving the SCR activity. CuCl₂(S₁₈)/TiO₂ catalyst showed simultaneous catalytic oxidation of Hg⁰ (73.9%) and NO (87%) at the temperature of 325 °C. Wang *et al.* [76] synthesized CeO₂ supported on anatase TiO₂ with high-energy facets and used it in the NH₃-SCR reaction. In the activity evaluation experiment, it was found that compared with Ce/P25 catalyst, it has high SCR activity. Through the characterization, it is concluded that the unique feature of the active energy (001) facet improves the thermal stability of CeO₂, and the presence of Ti³⁺ on the surface of TiO₂ effectively promotes the development of the SCR process, both of which lead to the remarkable catalytic performance for the catalyst. Chen *et al.* [77] studied the SCR activity of MnCe oxide-supported titanate nanotubes (TNT). And compared with the conventional MnCe/TiO₂ and V₂O₅/TiO₂ nanoparticle catalysts, it is found that MnCe/TNTs catalysts have higher SCR activity, sulfur and water resistance. The characterization results show that the BET surface area of MnCe/TNTs is larger, and the adsorption capacity of NH₃ is greatly enhanced, which is beneficial to the SCR activity. Liu *et al.* [78] designed the MnSmCo/Ti catalyst to simultaneously remove NO and Hg⁰ at low temperature. The experimental results show that the catalyst exhibits NO conversion rate of 80% and Hg⁰ removal rate of 100% at a gas hourly space velocity of 100,000 h⁻¹ in the temperature range of 150–250 °C. Li *et al.* [79] prepared a series of molybdenum (Mo)-modified vanadium (V)-based selective catalytic reduction (SCR) catalyst samples using the impregnation method to remove elemental mercury (Hg⁰) and nitrogen oxides (NO) at the same time. Through experiments, it is found that the metal loading and the order of impregnation have no effect on the denitration activity of the

catalyst, and have a particularly large effect on the mercury removal activity. The dipping sequence experiment found that MoO₃(7) + WO₃(3) → V₂O₅(0.5)/TiO₂ exhibited the highest mercury removal activity. The metal loading experiment found that V₂O₅(0.5) + MoO₃(7)/TiO₂ catalyst exhibited the highest mercury removal activity. Liu *et al.* [80] studied the simultaneous removal of NO and Hg with Sb-modified Mn/TiO₂ catalyst under low-temperature SCR conditions. The results show that the MnSb/TiO₂-0.25 catalyst can achieve NO removal (>90%) and Hg⁰ oxidation (> 80%) at 200–300 °C. Li *et al.* [26] studied The effect of flue gas composition on the removal of Hg⁰ and NO by a series of CeO₂ (ZrO₂)/TiO₂ catalysts. At 250–400 °C, the CeO₂(ZrO₂)/TiO₂ catalyst exhibited high Hg⁰ catalytic oxidation efficiency (> 95%) and high denitration efficiency (> 95%). Liu *et al.* [45] prepared Co/TiO₂ catalysts by the sol-gel method, and determined the optimal Co loading for Hg⁰ catalytic oxidation (7.5%). Yang *et al.* [81] prepared TiCe_{0.25}Sn_{0.25}O_x catalyst for synergetic removal of NO and Hg⁰ from flue gas. Through experiments they found TiCe_{0.25}Sn_{0.25}O_x has excellent NO and Hg⁰ removal performance, and also has satisfactory SO₂ tolerance, and revealed the synergistic removal mechanism and the effects of flue gas components on synergetic removal of NO and Hg⁰, as shown in Fig. 3a. Zhang *et al.* [82] loaded Co-Ce oxide on rod-like MnO₂ to simultaneously remove NO and Hg. They found that the Co-Ce/MnO₂ catalyst has excellent SCR activity and Hg capture efficiency. In addition, the Co-Ce/MnO₂ catalyst has a high tolerance to SO₂. Finally, the excellent activity and high sulfur resistance of the catalyst are explained through characterization techniques, as shown in Fig. 3b. Zhang *et al.* [83] researched Ce-Mo/TiO₂ catalyst to simultaneously remove NO and Hg. Ce-Mo/TiO₂-0.3 catalyst exhibited an excellent Hg⁰ oxidation and NO reduction efficiencies of over 90% at above 250 °C. In addition, Ce-Mo/TiO₂-0.3 catalyst also presented an excellent resistance to SO₂ and H₂O poisoning and a good stability and recyclability. The evaluation data of the catalytic activity of Ce-Mo/TiO₂ is shown in Fig. 3c. Liu *et al.* [84] found that loading Nb on MnTiO_x can significantly improve the conversion of

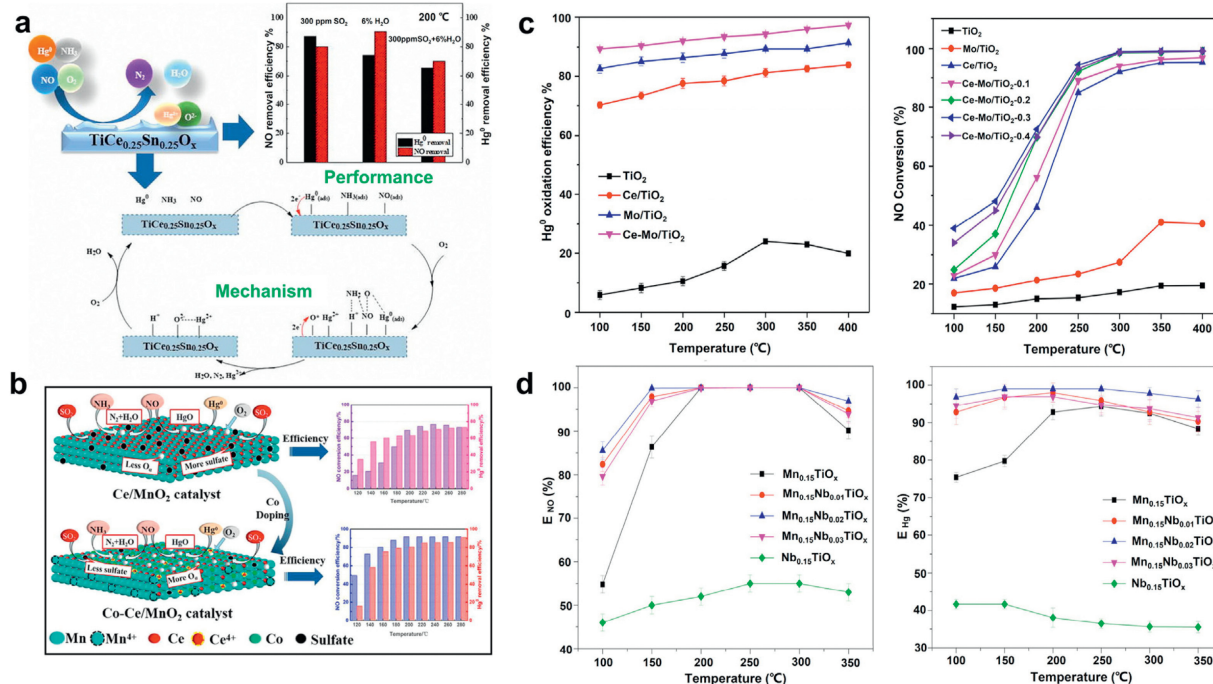


Fig. 3. (a) Synergetic removal of elemental mercury and NO over TiCe_{0.25}Sn_{0.25}O_x catalysts. Reproduced with permission [81]. Copyright 2019, Elsevier. (b) Simultaneous removal of NO and Hg⁰ in flue gas over Co-Ce oxide modified rod-like MnO₂ catalyst. Reproduced with permission [82]. Copyright 2020, Elsevier. (c) The Mo-Ce/TiO₂ catalyst

NO and the oxidation of Hg by the catalyst. The removal efficiency of different catalysts for NO and Hg are shown in Fig. 3d. In addition to TiO_2 , MnO_2 is also used as a carrier for simultaneous removal of NO and Hg^0 from flue gas.

As a stable crystalline powder, Al_2O_3 has good thermal stability, acid and alkali corrosion resistance, easy to form a fixed shape, and the surface area is less than $200 \text{ m}^2/\text{g}$. These ideal properties have attracted extensive attention in the field of simultaneous removal of SO_2 , NO_x , and Hg^0 . Wang *et al.* [47] prepared Cu and Fe-loaded Al_2O_3 catalysts for simultaneous removal of NO and Hg^0 . The characterization results show that Al_2O_3 as a support significantly increases the surface area and pore volume of the catalyst, improves the ability of the catalyst to adsorb gaseous reactants and therefore improves their catalytic efficiency. Moreover, Al_2O_3 increased the absorbed oxygen amount, indicating an increased number of active oxidative sites and a stronger oxidation ability for Hg^0 . Yue *et al.* [85] prepared a series of $\text{Cu}_3\text{Ce}_b\text{Zr}_c\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalysts by impregnation method to simultaneously remove NO_x and Hg^0 . Their research results show that 15% $\text{Cu}_{1.4}\text{Ce}_{0.55}\text{Zr}_{0.25}\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ has the highest removal efficiency of NO (93%) and Hg^0 (98%).

Silica based catalysts: Mesoporous silica has a large specific surface area, unique open-framework, a large pore volume and a high intrinsic surface activity, providing many adsorption sites for NO, SO_2 and Hg^0 . Chiu *et al.* [86] used the impregnation method to load V, Mn and Cu oxides onto SiO_2 to remove NO, SO_2 and Hg. The results show that the $\text{CuO}_x/\text{SiO}_2$ catalyst exhibits the greatest Hg^0 and NO removal performance. In addition, he also studied the removal of Hg^0 and NO by MnO_x impregnated $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2\text{-SiO}_2$ catalyst [87]. The catalysts loaded with 10% MnO_x showed the best activity for the removal of Hg^0 and NO. Liu *et al.* [49] loaded $\text{MnO}_x\text{-CeO}_x$ on SiO_2 to remove NO and Hg. Through the activity evaluation of different loadings of $\text{MnO}_x(a\%)\text{-CeO}_x(b\%)/\text{SiO}_2$, it is found that 20% $\text{MnO}_x\text{-10}\%\text{CeO}_x/\text{SiO}_2$ has the best catalytic activity, and its mercury removal efficiency is 96% at 100–300 °C. Secondly, they also found that the introduction of CeO_x can broaden the SCR activity temperature range of $\text{MnO}_x/\text{SiO}_2$ catalysts, as shown in Figs. 4a and b. Gu *et al.* [88] studied the catalytic NO removal efficiency of $\text{MnFeO}_x/\text{SiO}_2$ catalysts under different Fe/Si conditions. They found that adding an appropriate amount of FeO_x can significantly widen the temperature window of the catalyst. Li *et al.*

[89] prepared a $\text{TiO}_2\text{-SiO}_2$ photocatalyst for the catalytic oxidation of Hg. Studies have shown that the catalyst has excellent catalytic oxidation activity for Hg, and the Hg removal mechanism is summarized, as shown in Fig. 4c. Chen *et al.* [90] used the recycled Cu modified rice-husk-derived SiO_2 to remove NO and Hg. Studies have shown that 50% Cu/SiO_2 has the greatest Hg removal efficiency (88.2%), and 50% $\text{Cu-10}\%\text{Ce}/\text{SiO}_2$ has 85% NO conversion at 100–300 °C. Lin *et al.* [91] synthesized Cu-Mn-Ce oxide-incorporated Mesoporous Silica by hydrothermal exfoliation of silicate to remove NO and Hg. The research results show that Cu_2Mn_8 exhibits the highest Hg removal efficiency, and Ce doping can improve the NO removal efficiency.

3.1.3. Catalysts based on new supports

Molecular sieves-based catalysts: Zeolite-based materials have large specific surface area, good thermal stability, unique framework structure, excellent mechanical strength and adsorption, so they are considered as ideal carriers. Zeolite molecular sieves can chemically adsorb SO_2 , Hg and NO on the surface. The metal elements loaded on the surface of the zeolite molecular sieve and embedded in its pores can promote the oxidation or reduction of SO_2 , Hg and NO. Cao *et al.* [53] loaded Fe_3O_4 , silver and V_2O_5 on HZSM-5 by dipping. The experimental results show that at 150 °C, the removal rate of Hg by the catalyst is 97%, the removal rate of Hg^0 and NO is 80%. Finally, the mechanism of simultaneous removal of NO and Hg by the catalyst is explained, as shown in Fig. 5a. Yuan *et al.* [92] prepared nano-iron loaded ZSM-5 and combined vaporized H_2O_2 and $\text{Na}_2\text{S}_2\text{O}_8$, and $\text{Ca}(\text{OH})_2$ solution to simultaneously remove SO_2 , NO and Hg^0 . Their research results show that when the mass of the catalyst is 0.3 g, the removal rate of SO_2 , NO and Hg^0 reaches the highest, respectively 99.9%, 96.5% and 90.1%. Fan *et al.* [93] prepared $\text{Cu}/\text{HZSM-5}$ to simultaneously remove Hg^0 and NO. The experimental results show that the loading of copper significantly improves the activity of the catalyst, and the catalyst with a loading of 6% shows the best activity. Zhang *et al.* [67] used ZSM-5 modified with Mn-Fe to remove Hg at low temperatures and found that the introduction of Mn/Fe can effectively improve the mercury removal efficiency of ZSM-5. The catalyst with a Mn/Fe molar ratio of 1:2 has a 100% removal rate for Hg at 200–250 °C. Applying an immersion method, Chui *et al.* [51] used the CuCl_2/MCM prepared by the impregnation method is used

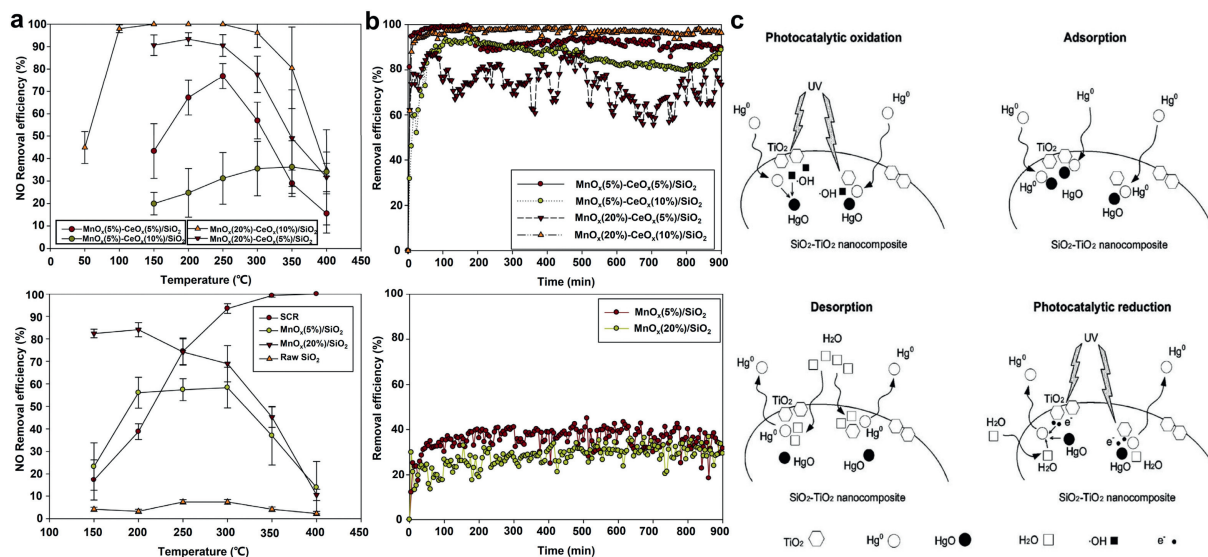


Fig. 4. (a) Removal of NO with $\text{MnO}_x\text{-CeO}_x/\text{SiO}_2$. Reproduced with permission [49]. Copyright 2017, Elsevier. (b) Removal of Hg^0 with $\text{MnO}_x\text{-CeO}_x/\text{SiO}_2$. Reproduced with permission [49]. Copyright 2017, Elsevier. (c) Mechanisms of Hg capture and reemission on the surface of $\text{SiO}_2\text{-TiO}_2$ nanocomposite. Reproduced with permission [89]. Copyright 2006, Elsevier.

for the simultaneous removal of SO_2 and NO. The experimental results show that the loading of CuCl_2 reduces the removal efficiency of SO_2 by 4%, but increases the removal efficiency of NO by 11%, as shown in Fig. 5b.

Silico-aluminum-phosphate (SAPO) is a microporous crystal composed of three kinds of tetrahedral units, namely, PO_4^{3-} , AlO_4^{5-} and SiO_2 . Its pore structure can be controlled by changing different synthesis conditions and silicon content [94,95]. SAPO are widely used as adsorbents, catalysts, and catalyst carriers. It is a new type of catalytic material with excellent shape selectivity, thermal stability and damp-heat stability. Because the framework is negatively charged, it has exchangeable cations and also exhibits proton acidity. SAPO can adjust the amount of acid by introducing various impurity atoms, so it can exhibit a catalytic performance ranging from medium strong acid to strong acid. It is well known that copper additives can improve the activity of SAPO-34, and copper-infused SAPO is very promising in industrial applications. Fickel *et al.* [94] showed that the NO conversion efficiency of Cu-infused SAPO approaches 100% at 200–400 °C. Wang *et al.* [50] found that the content of Si and Al affects the content of Cu^{2+} species on the Cu/SAPO-34 catalyst. In addition, the content of Si can affect the content of active sites (Si or Al) and the number of acid sites of the catalyst. To affect the SCR activity of the catalyst. Pang *et al.* [52] prepared Mn-exchanged SAPO-34 catalysts for low-temperature SCR of NO with NH_3 . Among their samples, 4 Mn/SAPO-34 achieved the highest SCR activity in the 120–210 °C temperature range. The characteristic results suggested that species related to Mn^{3+} and Mn^{4+} were the active sites of the catalyst.

MOFs-based catalysts: MOFs are intriguing porous materials with the advantage of adjustable pore size that are self-assembled by organic ligands and metal ions [96]. The adsorption performance of MOFs is boosted by sufficient porosity, large surface area, and versatile structure. In addition, MOFs promote the dispersion

of active components, providing a transportation channel for catalytic reactants. The metal centers in MOFs are evenly distributed and highly dispersed, concentrating their activity in certain catalytic reactions. The advantages of MOF carriers have been exploited in the removal of SO_2 , NO and Hg^0 from flue gas.

Wang *et al.* [97] prepared a MOF called MIL-100(Fe) and used it in the SCR reaction. Experimental results show that the NOx conversion rate of MIL-100(Fe) exceeds that of conventional $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$ catalysts below 300 °C. Zhang *et al.* [54] investigated the MnO_x -loaded MIL-100(Fe) was prepared by the impregnation method. The experimental results show that the catalyst supported by MIL-100(Fe) has higher Hg^0 adsorption and oxidation capacity than the catalyst supported by Fe_2O_3 at all test temperatures. The Hg^0 removal efficiency was 77.4% at 250 °C. In addition, the catalyst can be easily recovered from fly ash using magnets. The catalyst activity evaluation diagram and the removal mechanism diagram are shown in Fig. 6a. Zhang *et al.* [28] prepared Mn-Ce supported MOF (MnCe@MOF) catalyst by impregnation method. When removing Hg^0 and NO from the flue gas, the loading of Mn and Ce significantly enhanced the activity of the catalyst. Characteristic analysis shows that the MOF scaffold has a developed porous structure and a high surface area. This makes the active phase highly dispersed and thus enhances the activity of the catalyst. The sulfur and water resistance experiments show that MnCe@MOF has high resistance to SO_2 and H_2O . Fig. 6b shows the removal efficiency of Hg^0 and NO on the MnCe@MOF catalyst and the morphology of the catalyst. The stronger adsorption of Hg^0 and NH_3 on MOF catalysts than on conventional materials might be explained by the special structure and Lewis acidity of MOF [98,99].

PILCs-based catalysts: PILCs is a new type of catalytic material with a two-dimensional pore-like molecular sieve structure. Schematic representation of the clay structure is shown in Fig. 7a. It has the characteristics of adjustable pore structure,

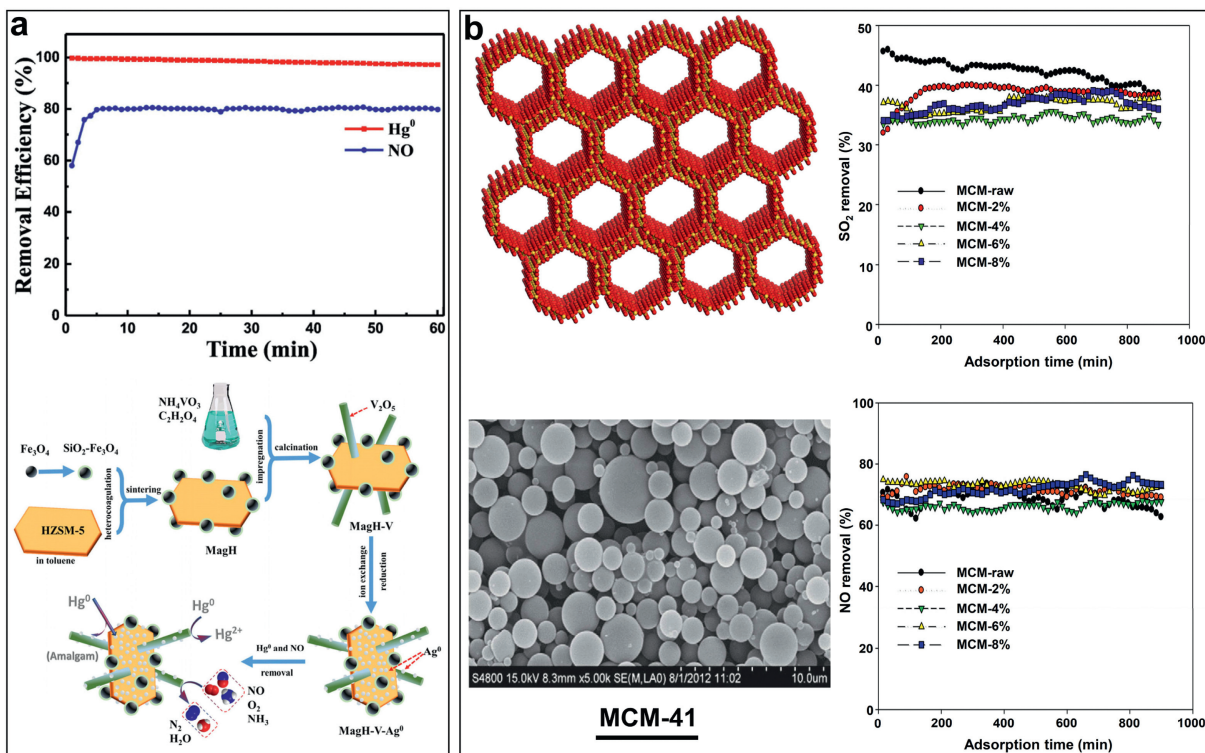


Fig. 5. (a) magnetically responsive catalytic sorbent and its use for removal of Hg^0 and NO. Reproduced with permission [53]. Copyright 2017, Elsevier. (b) The synergistic effect of CuCl_2 impregnated zeolites on simultaneous removal of Hg^0 , SO_2 and NO. Reproduced with permission [51]. Copyright 2014, Elsevier.

high porosity, high thermal stability, hydrothermal stability and exchangeable cations, so it is widely used to make catalysts and adsorbents [55,100–103]. Chae *et al.* [55] synthesized a novel SCR catalyst with a Ti-PILC support, which demonstrated higher performance than conventional catalysts. Shen *et al.* [24] innovatively loaded MnO_x in PILCs for low-temperature NH_3 -SCR denitration research. At the optimal loading of $\text{MnO}_x/\text{Ti-PILC}$ (10%) and 80 °C, the NO conversion efficiency approached 100%, with good H_2O resistance. Next, Shen *et al.* [104] systematically studied the low-temperature denitration activity of doped $\text{Mn-MO}_x/\text{Ti-PILC}$. They found that Ce and La additives promoted the denitrification activity [104]. He *et al.* [105] prepared a series of innovative Ce-Mn/Ti columnar clay (Ce-Mn/Ti-PILC) catalysts by the impregnation method for trapping elemental mercury (Hg^0) at 100–350 °C. The experimental results show that: in the temperature range of the study, the 6%Ce-6%MnO_x/Ti-PILC catalyst performance is greater than 90% Hg^0 removal rate. The activity evaluation data of the catalyst and the Hg removal mechanism are shown in Fig. 7b. It is found through experiments that in the first stage of the reaction, the main Hg^0 capture mechanism of the catalyst is adsorption. As the reaction progresses, the oxidizing ability of Hg^0 is greatly improved, which is contributed by the hydroxyl oxygen and lattice oxygen on the catalyst surface. Wang *et al.* [25] prepared a series of Mn-Ce/Ti-PILCs catalysts for

simultaneous removal of NO and elemental mercury in simulated flue gas. The experimental results show that 6%Mn-6%Ce/Ti-PILCs exhibit excellent NO conversion rate (> 95%) and Hg^0 removal efficiency (> 90%) at 250 °C. The characterization results show that the removal activity of NO and Hg^0 is strongly affected by the conversion between oxygen adsorbed on the catalyst surface and lattice oxygen. The ratio of $\text{Mn}^{4+}/\text{Mn}^{3+}$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$ on the surface of the catalyst affects the conversion rate of NO and the removal of Hg^0 . The modified PILC behaves like a catalyst support. The NO and Hg removal efficiencies from 100 °C to 300 °C are shown in Fig. 7c.

Catalyst with the same active component(s) shows very different activities in the simultaneous removal of SO_2 , NO and Hg^0 catalysts. Table 1 [24,25,28,47,49,54,64,65,69,75,80,82,106–111] lists the NO and Hg^0 removal efficiencies and SO_2 resistances of carriers with the same active components. Comparing the active metallic components among the carriers, we find that catalysts with Mn–Ce active sites are more resistant to SO_2 than catalysts with other metallic active sites. Therefore, catalysts with an Mn–Ce active component are potentially valuable in industrial applications. Furthermore, Mn–Ce@MOF is more SO_2 -resistant than Mn–Ce/ SiO_2 , possibly because the MOF specific surface area is higher in the former than the latter. Finally, we find that new supported catalysts are more SO_2 -resistant than catalysts based on conventional supports and unsupported catalyst.

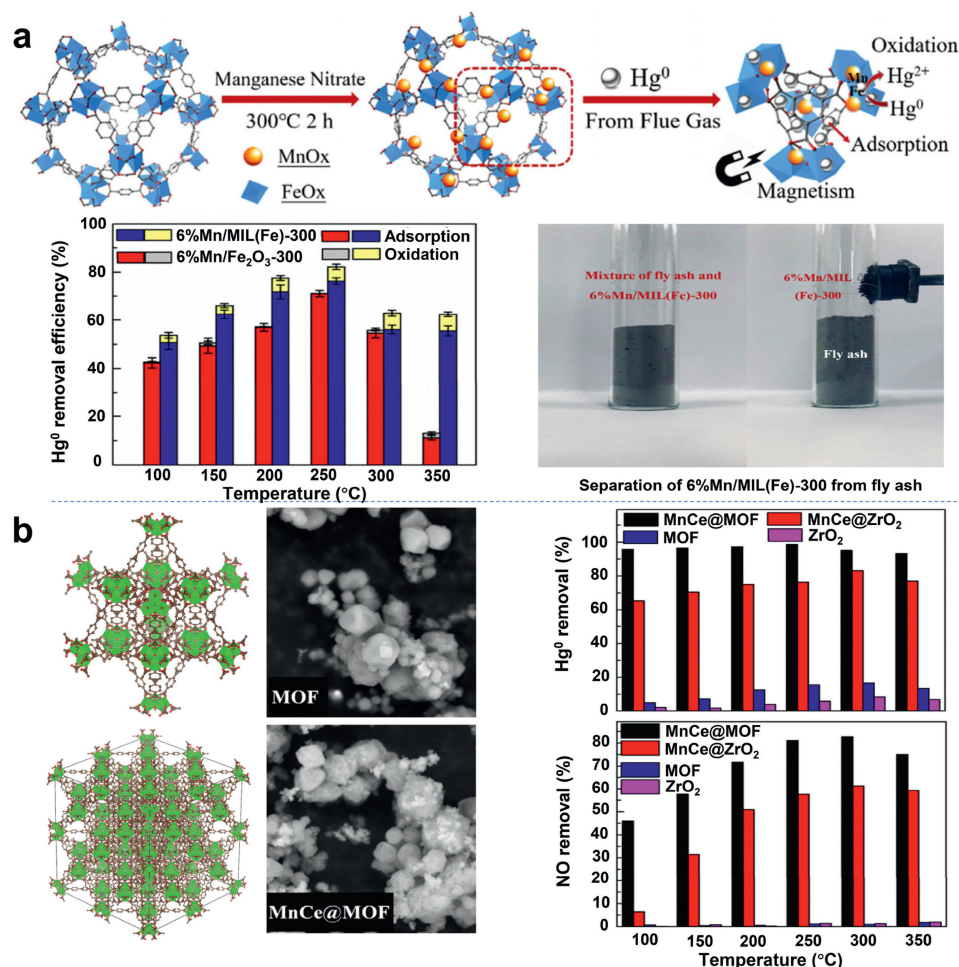


Fig. 6. (a) The catalyst activity evaluation diagram and the removal mechanism diagram. Reproduced with permission [54]. Copyright 2020, Elsevier. (b) The removal efficiency of Hg^0 and NO on the MnCe@MOF catalyst and the morphology of the catalyst. Reproduced with permission [28]. Copyright 2017, Elsevier.

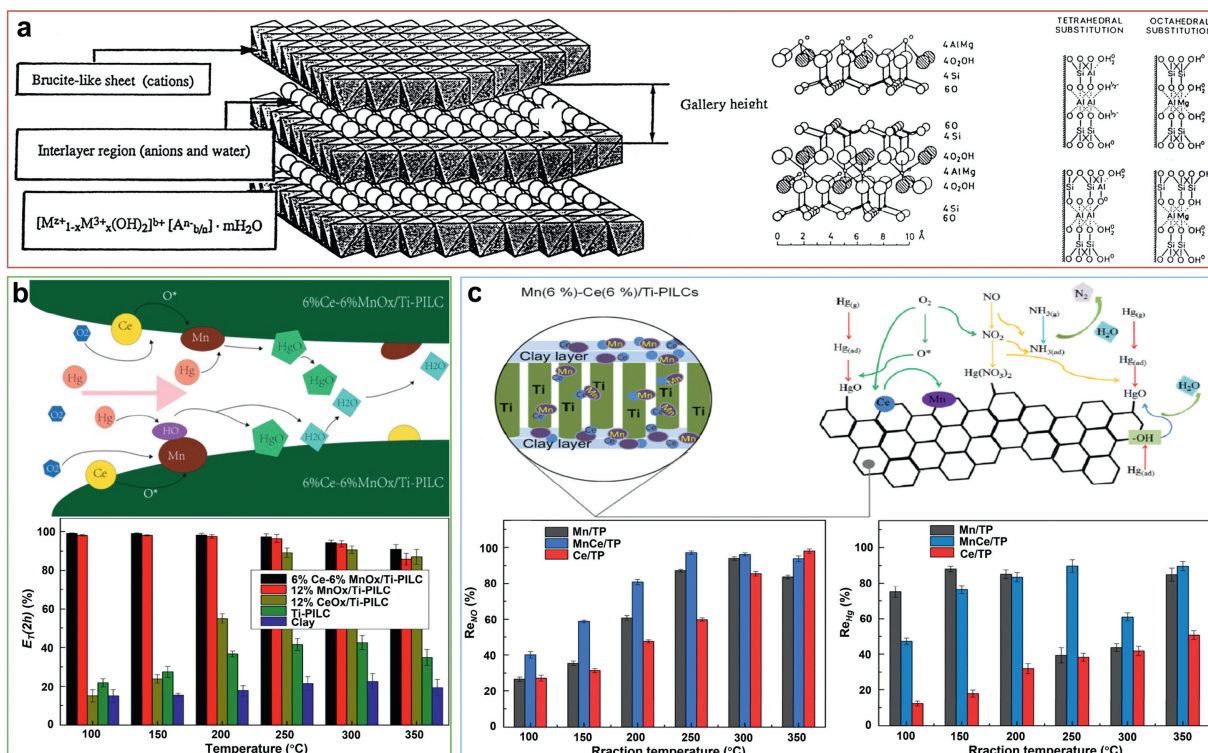


Fig. 7. (a) Schematic representation of the clay structure. Reproduced with permission [102]. Copyright 1998, Elsevier. (b) The removal effect of Ce-Mn/Ti-PILC on Hg and the removal mechanism diagram. Reproduced with permission [105]. Copyright 2014, American Chemical Society. (c) Simultaneous removal of NO and Hg by Ce-Mn/Ti-PILC and removal mechanism. Reproduced with permission [25]. Copyright 2015, American Chemical Society.

3.2. Influence of gas composition on removal effect

3.2.1. Single component effect

Real industrial exhaust gas contains species such as O_2 , NO, H_2O , NH_3 , HCl, and fly ash, whose concentrations depend on the industrial type and operational conditions. Because such variable gas concentrations remarkably affect the NO reduction and Hg^0

oxidation of catalysts, the impact of single flue-gas components on SO_2 , NO, and Hg^0 removal has attracted much interest.

Effect of O_2 : O_2 is an important component in the flue gas and plays a decisive role in most catalytic reactions [112,113]. Fig. 8a summarizes the effects of O_2 on SO_2 , NO, and Hg^0 . In the absence of O_2 , Hg can react with the chemisorbed and lattice oxygens on the catalyst surface. As the reaction proceeds, the limited oxygen on

Table 1

NO and Hg^0 removal efficiencies and SO_2 resistances of carriers with the same active components.

Catalyst	The components of simulated fuel gas	T (°C)	GHSV (h ⁻¹)	E_{NO} (%)	E_{Hg^0} (%)	SO_2 resistance	E_{NO} (%) (with SO_2)	Ref.
Cu-Ce/TiO ₂	1000 ppm NO, 1000 ppm NH ₃ , 300 μg/m ³ Hg ⁰ , 4% O ₂ , 200 ppm SO ₂	150–250	54,000	> 90	> 80	medium	> 70	[106]
Cu-Ce/V ₂ O ₅ -TiO ₂	500 ppm NO, 500 ppm NH ₃ , 30 μg/m ³ Hg ⁰ , 5% O ₂ , 1000 ppm SO ₂	200–400	45,000	> 97	> 75	weak	> 60	[107]
Cu-Fe/Al ₂ O ₃	700 ppm NO, 700 ppm NH ₃ , 12 ng Hg ⁰ , 4% O ₂ , 200 ppm SO ₂	150–390	100,000	90.4	66.9	medium	76	[47]
Cu-Fe/TiO ₂	700 ppm NO, 700 ppm NH ₃ , 12 ng Hg ⁰ , 4% O ₂ , 200 ppm SO ₂	150–390	100,000	86	65	medium	72	[47]
Cu-Fe/AC	500 ppm NO, 500 ppm NH ₃ , 30 μg/m ³ Hg ⁰ , 3% O ₂ , 200 ppm SO ₂	50–250	30,000	86	61	weak	60	[64]
Mn-Ce/SiO ₂	200 ppm NO, 30 ± 5 μg/m ³ Hg ⁰ , 6% O ₂ , 200 ppm SO ₂	80–320	8000	100	96	weak	10	[49]
Mn-Ce@MOF	500 ppm NO, 500 ppm NH ₃ , 35 μg/m ³ Hg ⁰ , 5% O ₂ , 300 ppm SO ₂	100–350	225,000	> 80	> 90	Strong	> 80	[28]
Mn-Ce/Ti-PILCs	500 ppm NO, 500 ppm NH ₃ , 50 μg/m ³ Hg ⁰ , 5% O ₂ , 100 ppm SO ₂	100–350	50,000	> 95	> 90	weak	> 30	[24,25]
MnO _x -CeO ₂	1000 ppm NO, 1000 ppm NH ₃ , 100 μg/m ³ Hg ⁰ , 2% O ₂ , 100 ppm SO ₂	50–350	60,000	98	> 80	weak	40	[108,109]
Mn/MIL(Fe)	500 ppm NO, 500 ppm NH ₃ , 35 μg/m ³ Hg ⁰ , 5% O ₂ , 500 ppm SO ₂	100–350	180,000	> 80	> 90	Strong	> 80	[54]
Mn/TiO ₂	400 ppm NO, 60–66 ppbv Hg ⁰ , 2% O ₂ , 200 ppm SO ₂	200	50,000	100	90	weak	40	[110]
Fe-Mn/TiO ₂	400 ppm NO, 400 ppm NH ₃ , 70 μg/m ³ Hg ⁰ , 4% O ₂ , 400 ppm SO ₂	100–350	100,000	97	65.6	medium	76.8	[111]
Ce-Co/MnO ₂	1000 ppm NO, 1000 ppm NH ₃ , 200 μg/m ³ Hg ⁰ , 5% O ₂ , 500 ppm SO ₂	200–300	10,000	97.9	91.9	medium	91.6	[82]
Ce-Co/BAC	600 ppm NO, 600 ppm NH ₃ , 100 μg/m ³ Hg ⁰ , 4% O ₂ , 400 ppm SO ₂	80–320	100,000	84.7	96.8	medium	80	[69]
FeCeOx/CNTs	1000 ppm NO, 1200 ppm NH ₃ , 100 μg/m ³ Hg ⁰ , 6% O ₂ , 500 ppm SO ₂	160–260	30,000	97.11	66.62	medium	81.67	[65]
CuCl ₂ (S ₁₈)/TiO ₂	500 ppm NO, 500 ppm NH ₃ , 70 μg/m ³ Hg ⁰ , 6% O ₂ , 500 ppm SO ₂	200–400	35,000	87	73.9	medium	83	[75]
MnSb/TiO ₂	500 ppm NO, 500 ppm NH ₃ , 75 μg/m ³ Hg ⁰ , 4% O ₂ , 100 ppm SO ₂	200–300	54,000	95	85	medium	78	[80]

the catalysts is gradually depleted, and the mercury removal efficiency is low. When O_2 is plentiful, the Hg^0 removal rate increases because the depleted lattice and chemisorbed oxygens are replaced with gas-phase O_2 [114,115]. Increasing the O_2 concentration does not significantly affect the Hg^0 removal efficiency. However, a large increase in O_2 concentration will increase the rate of SO_2 oxidation to SO_3 . The excessive generation of SO_3 will not be conducive to the progress of the SCR reaction, because it reacts with NH_3 and H_2O to produce ammonium sulfate and viscous ammonium bisulfate, gradually occupying the active sites of the catalyst and deactivating the catalyst.

Effect of NH_3 : NH_3 is one of the common reducing agents in industrial applications. The NH_3 content in the flue gas has a great influence on the reduction of NO and the oxidation of Hg^0 . Increasing the NH_3/NO ratio can promote the reduction of NO in the NH_3 SCR reaction, but the increase in NH_3 content will cause it to compete with Hg^0 for adsorption on the catalyst, thereby inhibiting the oxidation of Hg^0 [26,113,116]. Wang *et al.* testified that NH_3 inhibits Hg^0 oxidation over a $CuO-MnO_2-Fe_2O_3/\gamma-Al_2O_3$ catalyst [117]. However, other studies have reported a significantly positive effect of NH_3 on Hg^0 oxidation [118]. Li *et al.* [119] found that NH_3 consumes surface oxygen and limits the Hg^0 adsorption, thereby inhibiting Hg^0 oxidation over the catalyst. However, when the NH_3 supply is removed and O_2 is present, the inhibited Hg^0 oxidation activity is completely recovered. Therefore, adding O_2 at an appropriate concentration to a mixture of NO, SO_2 and Hg will preserve (to some extent) the Hg^0 oxidation by NH_3 . The mechanism by which NH_3 affects the SO_2 , NO and Hg^0 conversion is schematized in Fig. 8a.

Effect of H_2O : Water vapor is a main component in flue gases, and often leads to catalyst deactivation. Fig. 8a shows the effects of H_2O on SO_2 , NO, and Hg^0 . Water vapor decreases the Hg^0 oxidation and NO reduction over the supported catalyst [120], because it strongly competes with the reactive species for adsorption on the active sites of the catalyst [121]. When H_2O is removed from the simulated system, the efficiencies of NO reduction and Hg^0 oxidation are restored to some level slightly below the initial value.

Effect of HCl: HCl is regarded as the flue-gas component that most strongly affects the Hg^0 oxidation, because the main oxidized mercury species in coal-combustion flue gas is $HgCl_2$ [122]. Fig. 8a summarizes the effect of HCl on SO_2 , NO and Hg^0 . HCl is a critical oxidant for Hg^0 oxidation, especially by metal-based catalysts [123]. Although the introduction of HCl can significantly promote

the oxidation of Hg^0 , it cannot directly oxidize elemental mercury because it exists in a naturally reduced state [124]. Hg^0 oxidation by HCl requires the assistance of oxygen. According to several studies [125,126]. In the presence of HCl, HCl and O_2 will produce intermediate Cl_2 and active chlorine Cl^* on the catalyst, making the catalyst oxidize Hg^0 through the Chlor-Deacon process [127–129]. Wang *et al.* found that when present at low concentrations (10 ppm), HCl barely affects the NO conversion. However, at high concentrations, HCl prohibits the NO conversion because the chloride ions react with the metal on the catalyst surface, forming volatile metal-Cl compounds. These volatiles destroy the active sites and consequently deactivate the SCR reaction [130].

3.2.2. Interactive effect of SO_2 , NO and Hg^0

The above-mentioned flue-gas components are mixed with various pollutants (SO_2 , NO and Hg^0), which might influence each other during the catalytic reaction. Therefore, to simultaneously remove multiple pollutants, many researchers have investigated the interactive effects of SO_2 , NO, and Hg^0 during the pollutant-removal process. Their results are summarized in Fig. 8b.

Interactive effect of SO_2 and NO: The effect of SO_2 on NO removal in the SCR process is contentious. Some researchers [131,132] believe that SO_2 inhibits NO removal throughout the reaction system. Proponents of this view consider that SO_2 reacts with metal oxides and NH_3 in the presence of O_2 to form metal sulfates and ammonium sulfates (such as NH_4HSO_4 and $(NH_4)_2SO_4$). Especially, ammonium sulfates formed at low temperature on the catalyst surfaces occupy the active sites, lowering the SCR catalytic activity [133]. Other researchers [134,135] considered that the sulfate formed by SO_2 and metal oxides can enhance the acidity of the catalyst and help improve the low-temperature SCR activity of the catalyst, and some studies have found that introducing SO_2 into the SCR system can increase the removal rate of NO. Thus far, the influence of NO on SO_2 removal during the simultaneous removal of NO and SO_2 has not been investigated [14,136], possibly because the SO_2 reaction dominates over the NH_3 and O_2 reactions, meaning that NO does not affect the SO_2 removal.

Interactive effect of SO_2 and Hg^0 : The effect of SO_2 on Hg^0 removal from the flue gas is complicated and inconclusive. Both promotional and inhibitory effects are reported in the literature [39,137–139]. Li *et al.* [39] studied the effect of SO_2 on the oxidation of mercury on CeO_2-TiO_2 catalyst. Through experiments, it is found that in the absence of oxygen in the simulated flue gas, SO_2 greatly inhibits the

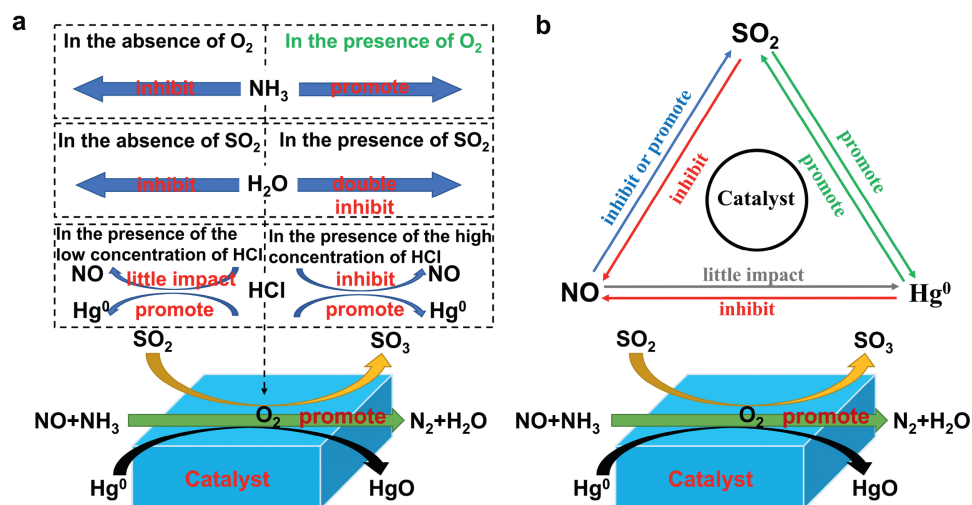


Fig. 8. (a) A diagram showing possible effect mechanism of O_2 , HCl, H_2O and NH_3 on SO_2 , NO and Hg^0 . (b) The interactive effects of SO_2 , NO and Hg^0 on the catalyst during the pollutant-removal process.

oxidation of Hg^0 , but once O_2 is introduced, SO_2 can promote the oxidation of Hg^0 . Tao *et al.* [140] explained the anoxic experimental phenomenon as competition by Hg^0 and SO_2 for similar active sites on the catalyst surface; therefore, when no O_2 exists in the flue gas, SO_2 inhibits the Hg^0 conversion. When O_2 is present, the oxidation of SO_2 to SO_3 is mediated by the chemisorbed oxygen generated by the Ce^{3+} -related charge imbalance on the catalyst. However, the effect of Hg on SO_2 removal appears to be unreported in the literature. We speculate that Hg affects SO_2 removal by the same process as SO_2 affects Hg removal.

Interactive effect of NO and Hg^0 : Wang *et al.* [15] studied the effect of NO on Hg^0 removal over an MnCe/TP catalyst. When the NO concentration increases from 200 ppm to 500 ppm, the removal efficiency of Hg^0 will slightly decrease. Wang believed that the Hg^0 oxidation was inhibited by other nonactive species such as nitrite, which might cover the active sites. Tao *et al.* [140] similarly found that in the absence of oxygen, increasing the NO concentration did not substantially change the Hg^0 removal efficiency. When O_2 was introduced to a flue gas containing NO, the Hg^0 removal efficiency slightly increased and a large amount of oxidized mercury was observed in the gas flow downstream of the sample. Li *et al.* [39] reported the same effect of NO on Hg oxidation over a CeTi catalyst. NO alone exerted a slightly propulsive effect on Hg^0 removal, especially at higher concentrations. The limited oxygen stored on the catalyst is consumed by both NO and Hg^0 oxidation [141]. The propulsive phenomenon [69] might be explained by weak NO absorption to the sample surface. Some of these absorbed NO might react with the O_2 on the metal–oxide catalyst surface, generating species such as NO^+ and NO_2 that can oxidize Hg^0 [142].

Whether the Hg^0 removal also affects NO removal is a pertinent question. Several researchers [25,69,112,143] who studied the effect of Hg^0 on NO removal reached a consensual conclusion: Hg^0

exerts only a slight effect on the reduction of NO. The inhibitory effect has been attributed to two possible causes. First, Hg^0 might compete with NO and NH_3 for adsorption to catalytic sites [69]. Second, the oxidation reaction of Hg^0 might accumulate HgO on the sample surface. If the accumulated Hg^0 covers some active sites, the NO removal efficiency will be slightly reduced [23,106,112,144].

3.3. Removal mechanism

Because the supported catalyst carrier generally has a rich specific surface area and a good pore structure, the supported active component is evenly dispersed on the surface and through the pores of the carrier. A supported catalyst ensures high catalytic activity for flue-gas removal. Thus far, no complete SO_2 , NO, and Hg^0 removal mechanism has been proposed. The mechanism of removal of SO_2 , NO and Hg^0 under the catalyst action is summarized in Fig. 9. The pathways of SO_2 , NO and Hg^0 removal are demonstrated in Fig. 9 with equations.

4. Conclusions and prospects

This paper presented the modern supported catalysts used in the removal of SO_2 , NO and Hg^0 from flue gas. The advantages and disadvantages of the formation technologies, the effects of crucial factors, and the removal mechanisms of the supported catalysts were carefully discussed. The technologies of carbon-based material adsorption technologies, photocatalytic oxidation technologies, wet scrubbing technologies, and NTP technologies face several problems: Large energy consumption, large equipment footprint, and secondary pollution. Solid-catalytic technology, which allows higher utilization of apparatus, incurs lower

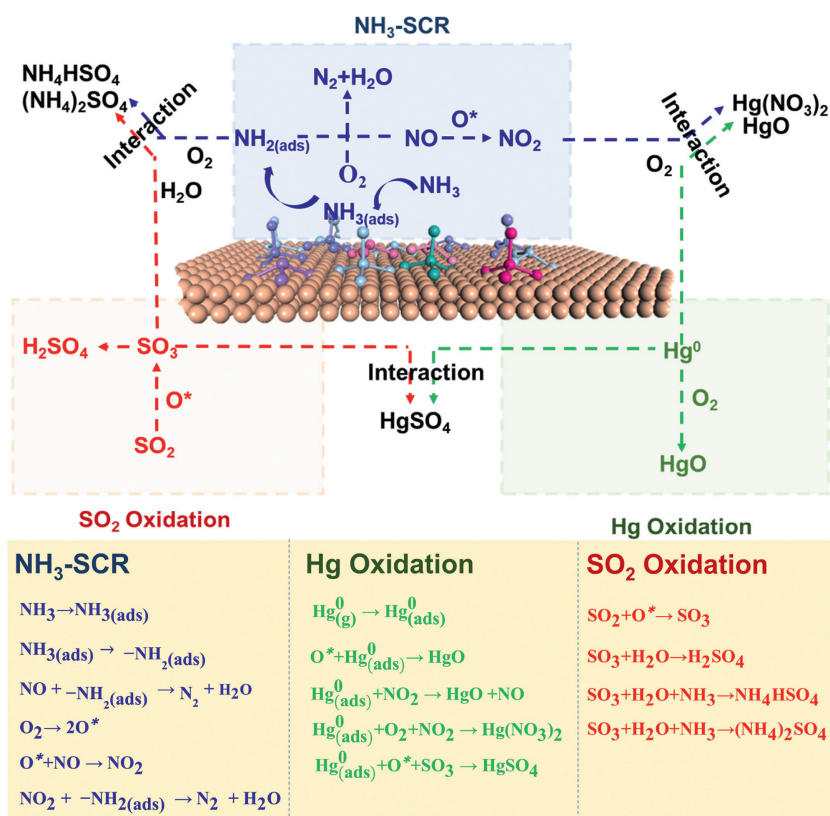


Fig. 9. The mechanism of synergistic removal of SO_2 , NO and Hg^0 by catalysts. The adsorbed surface oxygen is indicated as O^* .

operating costs, and requires less investment than multi-pollutant simultaneous removal technologies, has been widely investigated, and many supported catalysts have been researched in the past decade. MOF carriers for the low-temperature removal of NO and Hg⁰ provide much higher SO₂ resistance than traditional supported catalysts (carbon-based materials, metal oxides, and silica). In addition, the composition of real flue gas is very complicated and remarkably affects the NO reduction and Hg⁰ oxidation. The removal efficiencies of NO, SO₂ and Hg⁰ are enhanced in the presence of O₂. NH₃ inhibits Hg⁰ oxidation and NO reduction in the absence of O₂, but promotes these reactions in the presence of O₂. H₂O inhibits Hg⁰ oxidation and NO reduction by competitively adsorbing to the active sites. After exploring the surface chemical processes, this review clarified the mechanisms of SO₂, NO and Hg⁰ removal, and proposed a theory of catalytic multi-pollutant purification by new supported catalysts. Reviewing the past solid catalytic technology and the current technological development direction, we finally proposed the future research direction. At present, catalysts based on new supports have advantages in sulfur resistance and denitrification and mercury removal compared with catalysts based on conventional supports. Among the catalysts based on the new carrier, the new MOFs material as the carrier has higher sulfur resistance at low temperature than other traditional materials such as carbon materials and metal oxides. This is because its regular pore structure and large surface area make the supported metal oxides highly dispersed. Compared with other materials, its sulfur resistance is poor at high temperature. This is because the thermal stability of MOFs at high temperatures is poor. The molecular sieve material has a synergistic removal effect of thimerosal compared to other materials at high temperature. In summary, the high-temperature activity of MOFs-based supported catalysts and the low-temperature activity of molecular sieve-based supported catalysts are worthy of in-depth study in the gas purification technology for removing SO₂, NO_x and Hg⁰ from industrial exhaust gas.

Declaration of competing interest

The authors declare no competing financial interest.

Acknowledgements

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