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Abstract: As a clean fuel combustion technology, the circulating fluidized bed (CFB) has been developed rapidly in recent years, but one of its disadvantages is high N₂O emissions. With the implementation of increasingly strict pollution control standards, N₂O decomposition and removal technologies have become the main focus of current research. This paper reviews the latest research on noble metals, metal oxides, the molecular sieve and other new catalysts and decomposition methods for N₂O removal. The research methods and functions of catalysts are compared and the existing problems are summarized. The future directions of development in N₂O decomposition and removal are considered. Noble metals and the molecular sieve show satisfactory activity at relatively low temperatures, but their catalytic efficiency is obviously hindered by O₂, NO and H₂O. In addition, high costs and insufficient thermal stability limit their widespread industrial application. The metal oxide catalytic technology, especially oxygen carrier-aided combustion (OCAC), is expected to be the ideal method for N₂O removal in CFB boilers due to its stability and economical feasibility.

Keywords: CFB; fuel; metal oxide; N2O decomposition; OCAC



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). 1. Introduction

Carbon is a resource with huge reserves in China and is mostly used in direct combustion [1]. Although China is rich in various types of carbon resources, the proportion of low-quality carbon such as high ash is large. Meanwhile, carbon gangue, slime and other low-calorific-value by-products are produced in the process of coal mining and processing. Therefore, its clean and efficient combustion is of great significance in the field of energy [2].

CFB combustion technology is an economic and effective clean carbon combustion technology [3,4]. Due to its advantages of strong fuel adaptability, high combustion efficiency, low operational costs and low pollutant emissions, it has been developed rapidly and has been widely used in recent years, offering a solution to the problem whereby the above inferior fuel is difficult to apply effectively in the traditional pulverized carbon combustion technology [5,6].

At present, in China, the CFB boiler occupies an internationally advanced level in terms of installed capacity, application quantity and pollution control [7]. By the end of 2020, 48 supercritical CFB boiler units were in service, including 3 units of 600–660 MW and 45 units of 350 MW [8].

Due to the low combustion temperature, the CFB boiler creates high N_2O emissions [9]. N_2O exists in the atmosphere for a long time, up to 120 years [10]. Its contribution to the greenhouse effect is 2.5 times that of CH₄ and 310 times that of CO₂ [11]. Due to its long residence time in the atmosphere and serious greenhouse effect, it has a highly detrimental impact on the atmosphere [11]. It also exacerbates the ozone hole, growing at a rate of 0.2% per year. With the introduction of the latest national ultra-low pollution emission standard, the CFB boiler is facing strong pressure regarding pollutant emission

reduction [12]. Effectively controlling and reducing N₂O emissions has become an urgent environmental problem to be solved.

The mainstream emission reduction methods for N₂O include high-temperature decomposition, catalytic decomposition, selective removal, improvement of combustion processes, etc. [13]. Among them, catalytic decomposition has become a promising N₂O removal technology due to its many advantages. Its operation cost is very low and the process is simple. Moreover, its decomposition products are clean, with no secondary pollution to the environment and no CO₂. Equation (1) is the overall decomposition reaction of N₂O [13].

$$2N_2O \rightarrow 2N_2 + O_2(H^o_{298} = -163 \text{kJ/mol})$$
 (1)

N₂O sources include adipic acid production, nitric acid production, fossil fuel and biomass combustion and vehicle emissions [14]. Noble metals, the molecular sieve, metal oxides and other types of catalysts can produce certain effects on N₂O decomposition [15]. Noble metals are mainly used in nitric acid production and vehicle exhaust emissions; there are many kinds of metal oxides, which are widely used in the above fields. The molecular sieve can be used in the petrochemical and acid industries [16,17]. CFB boilers have broad prospects in the combustion of inferior fuel and biomass [4]. Therefore, it is preferable to consider metal oxide catalysts, with low costs and good stability under the main combustion temperature range of CFB and complex environment conditions [18].

Scholars have conducted a large amount of research in this area and made great progress [19–22]. Noble metals show good catalytic performance at low temperatures, and the molecular sieve shows good catalytic activity and environmental tolerance, but their costs are high, the preparation process is complex, and the catalytic efficiency is hindered by O_2 , NO and H_2O [23]. Compared with the above catalysts, metal oxide catalysts not only have low costs and good thermal stability, but also have excellent redox performance and high N₂O catalytic decomposition activity, making them very promising catalysts [18]. Interestingly, mixed metal oxides composed of two or more specific proportions of a single oxide can exhibit completely different structural, electronic and chemical properties to the parent oxide. However, there are limited reports on the progress of N₂O catalytic decomposition, but the development of highly active, stable and low-cost catalytic materials requires an overall understanding of the catalyst, which is very important for the effective control of N₂O emissions from industry and energy.

Therefore, this paper summarizes the research progress regarding N_2O decomposition in recent years and introduces the structural characteristics of various catalysts (noble metals, the molecular sieve, metal oxides, etc.) and the effects of catalyst support, preparation methods and reaction conditions on catalyst performance. Meanwhile, we also discuss the advantages and disadvantages of catalysts in detail, so as to provide ideas for subsequent research on N_2O decomposition catalysts. The future research directions regarding N_2O catalytic decomposition are also proposed.

2. The Noble Metal

The noble metal is the earliest N₂O catalytic remover and includes Rh, Ru, Pd, Pt, Au, In, etc. [24–26]. They are usually supported on porous carrier materials in the form of ions or a single metal [27,28]. Porous materials mainly include Al_2O_3 , MgO, SiO₂, TiO₂ and ZrO₂ [29,30]. The performance of a catalyst is not only related to the type of active components, but also to the type and structure of the support used [31–35].

2.1. Catalytic Mechanism

There are two typical mechanisms involved in the action of noble metal catalysts on N_2O : the Kondratenko mechanism and the Hinshelwood mechanism. According to the Kondratenko mechanism [25], N_2O is reversibly decomposed into N_2 and adsorbed oxygen on the surface through Formula (2). The adsorbed oxygen reacts with N_2O through Formula (3) to produce N_2 and O_2 , which is irreversible. Therefore, the mechanism considers

that half of the O_2 comes from adsorbed oxygen and half from N_2O . The Hinshelwood mechanism [36] posits that O_2 comes from adsorbed oxygen. N_2O forms adsorbed N_2O on the Pt surface through Formula (4), which is then decomposed into nitrogen and adsorbed oxygen, and the adsorbed oxygen is combined to form O_2 [36].

$$N_2O + s \rightarrow N_2 + O - s \tag{2}$$

$$N_2O + O - s \rightarrow N_2 + O_2 \tag{3}$$

$$N_2O + s \to N_2O - s \tag{4}$$

$$N_2O - s \rightarrow N_2 + O - s \tag{5}$$

$$2O - s \rightarrow O_2 + 2s \tag{6}$$

2.2. Research Progress

Rh, Ru, Pd, Pt, Au and In show certain catalytic activity for the decomposition of N₂O, and Rh displays the highest activity [37,38]. Doi et al. [38] prepared Rh/Al₂O₃, Pd/Al₂O₃ and Pt/Al₂O₃ catalysts for the N₂O decomposition reaction, as shown in Figure 1. The N₂O catalytic decomposition activities were in the following order: Rh/Al₂O₃ > Pd/Al₂O₃ > Pt/Al₂O₃. Aviles et al. [39] simulated the change in bond energy in N-N under the condition of containing Rh as the active component of the catalyst by means of quantum chemistry. Marco et al. [40] studied the decomposition performance of a Rh-based catalyst for N₂O. The results showed that when the Rh content in the catalyst was 1%, it had excellent decomposition performance for a high concentration of N₂O.



Figure 1. Dependence of catalytic N₂O decomposition on reaction temperature [38]. Reprint with permission [38]; 2001, Elsevier.

Hans et al. [41] studied the effects of particle size and support on the activity of a Rh catalyst, and prepared a series of Rh-supported catalysts, such as MgO, TiO₂, SiO₂, CeO₂ and Al₂O₃ (diameter 0.5–4.0 nm). It was found that when the average particle size was 2.1–2.4 nm, Rh/MgO and Rh/SiO₂ showed good low-temperature activity and the activity temperature window was 200–300 °C in an aerobic environment. Rh particle size is the main factor affecting catalyst activity, and the redox capacity of the active components is a secondary factor. Figure 2 shows the conversion achieved using a Rh(N)/MOx catalyst in an aerobic environment. According to the temperature required to achieve 50% conversion (T₅₀), the overall activity of the catalyst has the following order: Rh(N)/MgO (T₅₀ = 249 °C)

100 80 Conversion of N,0(%) 60 Rh/Mg0 40 Rh/SiO, Rh/CeO, Rh/Al20 20 Rh/Ti0 Ô 150 200 250 300 350 400 450 500 100 Temperature (°C)

 $\approx \text{Rh}(\text{N})/\text{SiO}_2 \text{ } (\text{T}_{50} = 249 \text{ }^\circ\text{C}) > \text{Rh}(\text{N})/\text{CeO}_2 \text{ } (\text{T}_{50} = 289 \text{ }^\circ\text{C}) > \text{Rh}(\text{N})/\text{Al}_2\text{O}_3 \text{ } (\text{T}_{50} = 341 \text{ }^\circ\text{C}) \\ \approx \text{Rh}(\text{N})/\text{TiO}_2 \text{ } (\text{T}_{50} = 342 \text{ }^\circ\text{C}).$

Figure 2. Decomposition of N₂O by Rh catalysts in aerobic environment [41]. Reprint with permission [41]; 2011, Elsevier.

Parres et al. [42] supported noble metals on γ -A1₂O₃ and pure CeO₂ to prepare catalysts with high activity. At 300 °C, the decomposition efficiency of the Rh-supported catalyst could reach more than 98%. The activity of noble metal catalysts is also closely related to the properties of the support. For example, the catalytic activity of Rh/CeO₂ is significantly higher than that of Rh/ γ -A1₂O₃.

2.3. Effect of Support

The N₂O decomposition activity of a noble metal catalyst is closely related to the type of support. Hussain et al. [43] compared the activity of Rh of MCM-41, KIT-6, SBA-15 spherical and SBA-15 conventional catalysts and found that the SBA-15 spherical catalyst not only exhibited the highest activity, but also had the best anti-aging impact and long-term stability.

Lin et al. [44] studied the activity of RhOx/M-P-O (M = Mg, Al, Ca, Fe, Co, Zn, La) catalysts for N₂O decomposition under oxygen conditions. The activity increased in the order of RhOx/Zn-P-O \approx RhOx/Fe-P-O < RhOx/Al-P-O < RhOx/Co-P-O < RhOx/Mg-P-O < RhOx/La-P-O < RhOx/HAP, indicating that the supports had significant effects. Among these catalysts, RhOx/HAP showed the highest activity. RhOx/HAP has small RhOx particles (average 1.2 nm), rich basic sites (104.1 µmol/g), abundant surface hydroxyl groups, and it can easily desorb O₂ from RhOx/HAP at relatively low temperatures. These characteristics make RhOx/HAP the most active catalyst among RhOx/M-P-O catalysts. Different supports can affect the size of RhOx particles are not the only factors affecting the catalytic activity. The relatively rich basic sites, O₂ adsorption sites and surface hydroxyl groups also play an important role [45].

Figure 3 shows the activity of different mesoporous silica-supported Rh for N_2O decomposition. The Rh-MCF catalyst demonstrates the highest activity [40]. MCF-type materials have three-dimensional mesopores with very large cavities, so that small, diamond-shaped particles are evenly distributed on the inner surface area.





Dou et al. [46] explored the N_2O catalytic decomposition performance of modified noble metal catalysts at different pH values. Although the activity of the two modified catalysts was good, the conversion decreased in varying degrees after 10 h in the presence of O_2 and steam.

The noble metal can show good N_2O decomposition performance at low temperatures, so it has been used since the 1970s. However, because of its high cost, narrow temperature window and the risk of poisoning due to the inhibition of oxygen and water vapor, its large-scale application in industry is limited [47].

3. The Molecular Sieve

The molecular sieve catalyst is a silicon aluminum salt catalyst with a uniform pore structure and strong ion exchange performance [48]. It has been of great interest in the field of catalyst research and attracted extensive attention because of its non-toxic nature, lack of pollution, high activity and wide temperature window [49].

3.1. Research Progress

The molecular sieve catalyst is mostly based on transition metals, such as Fe, Cu, Mn, Co, Ni, Ce, etc. [50–53]. A large number of scholars have studied the existing molecular sieves, such as ZSM-5, ZSM-11, USY, beta, etc. [54–58]. The molecular sieve generally has a large specific surface area, uniform pore size, regular pore structure and high selective surface, which can make the active components loaded on its surface highly dispersed, thus increasing the active site of the catalyst.

Guzman et al. [59] prepared Fe-BEA, Fe-FER and Fe-ZSM-5 by the ion exchange method. It was found that the properties of the main molecular sieve had a great impact on the activity of Fe species, and the activity of Fe-FER was the best.

Wu et al. [60] prepared iron-based molecular sieves pretreated with nitric acid for different times. It was found that long-term acid treatment affected the catalytic performance of Fe-ZSM-5 samples and the activity increased slightly with the extension of the acid treatment time. The catalytic performance of the Fe-beta sample showed the clearest improvement. The increase in catalytic activity could be explained by the increase in active iron loading caused by structural changes.

Smeets et al. [61] prepared Co-ZSM-5 catalysts with different Co content and studied the effects on catalyst activity. It was found that the oxidized cobalt species did not contribute significantly to the catalytic decomposition of N_2O , but monatomic Co showed high catalytic activity.

Meng et al. [62] performed a decomposition reaction experiment using a Cu ion molecular sieve catalyst for N_2O . As shown in Figure 4, the results showed that when

the Cu content was 3% (Silicalite-1@Cu-ZSM-5), the catalyst had the best decomposition activity, but when the flue gas contained oxygen and water vapor, its decomposition activity decreased. Silicalite-1@Cu-ZSM-5 had more dimetric Cu ions upon thermal pretreatment in He. In addition, less O₂ could be adsorbed on Silicalite-1@Cu-ZSM-5. Both factors contributed to the much higher activity of Silicalite-1@Cu-ZSM-5.



Figure 4. N₂O conversion over Silicalite-1@Cu-ZSM-5(#1) and Cu-ZSM-5(#2) [62]. Reprint with permission [62]; 2015, Elsevier.

Kondratenko et al. [63] studied the catalytic effect of Fe and Rh supported on the molecular sieve ZSM-5 on N_2O . The two catalysts were prepared by different methods. It was found that the O_2 desorption paths of the two modified ZSM-5 molecular sieves were different. The adsorption of N_2O by Rh species was significantly stronger than that by Fe species, and it had higher catalytic activity (below 623 K).

3.2. Effect of the Preparation Method

The preparation method has a great impact on molecular sieve catalysts; the methods include wet ion exchange, isomorphic substitution, solid-state ion exchange and chemical vapor deposition [64]. Compared with other methods, wet ion exchange is simpler and more feasible. The pH value of the suspension and the degree of ion exchange are the key factors affecting the activity of the catalyst [64].

Panov et al. [65,66] determined that the iron-based molecular sieve is one of the most active catalysts for the decomposition of N_2O . Compared with the catalysts prepared by chemical vapor deposition, the iron-based molecular sieve catalysts prepared by wet ion exchange not only have higher N_2O decomposition activity, but also better hydrothermal stability. The metal cations outside the skeleton are considered to be the active center.

Du et al. [67] studied the effects of preparation methods and types of precursors on the activity of a Rh/SBA-15 catalyst. The results showed that the activity of the catalyst was closely related to the preparation method of the catalyst and the size of its precursor. The activity change trend corresponded well with the dispersion state of Rh on SBA-15, i.e., the better the dispersion, the higher the activity.

Compared with noble metal catalysts, metal-ion-modified molecular sieves have the advantages of higher activity and better low-temperature activity [68]. However, in the presence of high-temperature water vapor, the collapse of the molecular sieve structure and irreversible deactivation can easily occur, which can affect the activity of the catalyst [69]. Therefore, it is necessary to further improve the catalytic performance and hydrothermal stability of the molecular sieve by pretreatment and surface modification.

4. The Metal Oxide

Metal oxide catalysts have high catalytic activity for N₂O decomposition and mainly include transition metal oxides (Fe₂O₃, NiO, Co₃O₄, CuO, etc.), alkaline earth metal oxides (CaO, BaO, MgO, etc.), rare earth metal oxides (La₂O₃, CeO₂, etc.) and their composite metal oxides [70–74].

4.1. Single Metal Oxide (Bare Oxide)

In the presence of oxygen, Ohnishi et al. [71] studied the activity of various metal oxide catalysts, i.e., NiO, Co_3O_4 , CuO and MnO_2 , in the N₂O decomposition reaction. NiO and Co_3O_4 showed strong low-temperature activity. The preparation conditions had little effect on the activity of the NiO catalyst, but the activity of the Co_3O_4 catalyst depended strongly on the preparation conditions, and the residual sodium content in the precursor was the decisive factor affecting catalyst activity.

Wu et al. [75] studied the effect of CaO on the decomposition of N₂O and the selectivity of its decomposition products. The results showed that CaO could catalyze the decomposition of N₂O, and the selectivity of N₂ was higher than that of NO according to DFT. The possibility of N₂O decomposition to produce N₂ is greater than that of the NO generation path. The structure and composition of single metal oxides are relatively simple, so they are more suitable for the study of the N₂O catalytic decomposition reaction mechanism.

Hou et al. [76] studied different metal oxides in a circulating fluidized bed and found that the catalytic capacity gradually decreased from Fe₃O₄, Fe₂O₃, CaO, MgO, Al₂O₃, CaSO₄ and SiO₂. Barisic et al. [77] observed that the higher the amount of catalytic active oxides (Fe₂O₃ + CaO + MgO + Al₂O₃) in a 12 MW circulating fluidized bed, the higher the activity of N₂O decomposition. The experimental results of Yang et al. [78] showed that iron and its oxides had a strong catalytic effect on N₂O, but the effect was greatly reduced when H₂O and O₂ were present in the environment. Figure 5 shows the catalytic activity of samples with different Fe content (1, 5 and 10%) for N₂O decomposition. At the reaction temperature of 550 °C, when the added iron content increased from 1% to 10%, the N₂O conversion increased from 17.7% to 66.3%. Therefore, the increase in iron content improved the decomposition rate of N₂O and promoted the overall transformation of N₂O. At 700 °C, the N₂O conversion could reach 100% in all cases. The catalyst activity increased with the increase in reaction temperature.



Figure 5. Effect of the active element content on N₂O conversion [78]. Reprint with permission [78]; 2010, Wiley.

4.2. Mixed Metal Oxide

The catalytic activity of mixed metal oxides can be significantly improved, and such catalysts have high thermal stability by stabilizing some active substances and adjusting the composition ratio [78]. Mixed metal oxide catalysts mainly include spinel oxide, hydrotalcite oxide, hexaaluminate oxide, cerium-based oxide, perovskite oxide, etc. [79,80].

The chemical formula of spinel oxide is AB_2O_4 . Russo et al. [81] produced a variety of AB_2O_4 spinel catalysts and found that the catalyst with Co at the B position had better catalytic activity, especially $MgCo_2O_4$.

Hydrotalcite oxide is a new material with a layered structure that is composed of a main cationic laminate and an anion-filled interlayer. Hydrothermal treatment and alkali metal salts have a significant effect on the catalytic decomposition of N₂O by hydrotalcite, but O₂ and CO have a negative effect on it. Pacultova et al. [82] studied the catalytic reduction of N₂O by CO on Co-Mn-Al calcined hydrotalcite and found that when there was no oxygen in the feeding gas, CO strongly promoted the conversion of N₂O. As shown in Figure 6, in the presence of O₂, CO acted as a non-elective reducing agent to inhibit the destruction of N₂O.



Figure 6. Temperature dependence of N₂O conversion [82]. Reprint with permission [82]; 2008, Elsevier.

Hexaaluminate oxide is a crystal with a hexagonal layered structure formed by the alternate stacking of spinel structural units and mirrors [79]. The chemical formula can be written as $AAl_{12}O_{19}$ and A can be an alkali metal, alkaline earth metal or rare earth metal. Santiago et al. [83] synthesized hexaaluminate LaFeAl₁₁O₁₉ with a high specific surface area via the carbon template method. The use of the carbon template increased the surface area and improved the catalytic performance. There was a quasi-linear relationship between the reaction rate and the specific surface area of the sample. Catalytic high-temperature decomposition (secondary abatement) of nitrous oxide over calcium aluminate 12CaO center dot 7Al(2)O(3) (mayenite) was studied the model laboratory tests (TPSR) and pilot units (steady-state) using a real feed by Ruszak et al. [84]. It was found that the catalyst exhibited high efficiency and selectivity in N₂O removal, reaching practically 100% conversion at 1150 K, without appreciable total losses of NOx. A hexaaluminate catalyst has a large specific surface area at high temperatures, with excellent sintering resistance and thermal shock resistance. It is a good high-temperature, thermally stable material, so it is the most promising high-temperature N₂O decomposition catalyst.

Xue et al. [85] prepared a series of Co-based mixed metal oxides and found that the activity of the Co-Ce mixed oxide catalyst was the best. Its activity was related to the molar ratio of Ce/Co. The addition of Ce improved the catalytic ability by increasing the specific surface area of the catalyst and the redox ability of the active site.

The chemical composition of perovskite oxide can be expressed as ABO₃. A is usually rare earth metal ions with a large radius, while B is transition metal ions with a small radius. It has the characteristics of stable structure, strong chemical adsorption capacity and good oxygen migration and storage capacity, which result in good catalytic performance [86]. Dacquin et al. [87] et al. prepared LaCoO₃ through different preparation methods to explore its catalytic decomposition effect on N₂O. It was found that different surface compositions may change the subsequent interaction between the surface and reactants and the related catalytic properties. LaCoO₃ prepared by reactive grinding is considered to be the most active catalyst because of its high specific surface area, but the presence of Fe and Zn impurities inherent in the preparation method can interfere with the catalytic performance.

4.3. Oxygen Carrier-Aided Combustion (OCAC)

In a CFB boiler, one of the basic functions of the bed material is to transfer heat between different parts of the boiler to reduce the thermal gradient and make the operation stable. In order to enhance the heat transfer and uniform heat distribution, inert fluidized bed materials, such as silica sand, are usually used. Partial or total replacement of silica sand with an oxygen carrier may help to promote the oxygen distribution in the combustion chamber, which is referred to as oxygen carrier-aided combustion (OCAC) [88]. An oxygen carrier is a kind of metal oxide that not only transmits heat through a chemical redox reaction, but also transmits oxygen between oxygen-poor and oxygen-rich areas of the boiler. It has the ability to alternately absorb and release oxygen, so as to improve the distribution of oxygen in the whole furnace. Therefore, OCAC can be considered to be used for N_2O emission reduction in CFB boilers.

Carl et al. [88] examined silica sand under the same combustion conditions using a synthetic material mixture of three alternative bed materials, namely manganese ore, ilmenite and Fe_2O_3 on a zirconia support. The results showed that the content of carbon monoxide in the exhaust gas can be reduced by using an activated bed material in the combustion process when using a sub-stoichiometric air–fuel ratio.

Fredrik et al. [89] investigated the use of slag as an oxygen carrier in a 12 MW boiler. Bed material samples were studied in a laboratory fluidized bed reactor to determine reactivity changes in common volatile fuel components (i.e., carbon monoxide, H_2 , methane and C_6H_6). It was found that slag could be used as an oxygen carrier in the combustion of biofuels, but the reactivity of syngas, CH_4 and C_6H_6 decreased with time.

Wang et al. [90] used a small fluidized bed reactor to simulate the fuel conversion and nitric oxide generation of OCAC and tested four oxygen carriers, two ores (ilmenite and manganese ore) and two oxide scales (expressed as AQS and LDST). They used charcoal as fuel and monitored the concentration of carbon dioxide, carbon monoxide, methane, oxygen and nitric oxide in the waste gas. The results showed that the use of an oxygen carrier reduced the emission level of carbon monoxide and improved the combustion efficiency. The improvement in combustion efficiency could be attributed to the reactivity of the oxygen carrier with carbon monoxide to a great extent. OCAC can reduce the level of excess air, thereby reducing the emission level of nitric oxide.

Thunman et al. [91] found that after adding ilmenite into silica sand, the concentrations of carbon monoxide and nitric oxide decreased by 80% and 30%, respectively, in a 12 MW CFB boiler. The addition of ilmenite reduced the concentration of carbon monoxide and total hydrocarbons in a cross-section of the furnace.

A possible problem is that, in the case of coal or any ash-containing fuel, there may be an interaction between its derived ash and the oxygen carrier, which may lead to the deactivation and agglomeration of the oxygen carrier. Esraa et al. [92] studied the interaction between common oxides in ash and copper oxide oxygen carriers in terms of both experimental and thermodynamic aspects. CuO is a widely used oxygen carrier that can release gaseous oxygen in an inert atmosphere. SiO₂, Al₂O₃, Fe₂O₃, CaO and K₂O were used to represent the oxides in ash. In all cases, large amounts of copper oxide survived without any interaction. Silicate base layers, especially potassium silicate, lead to strong agglomeration, which is likely to reduce the service life and oxygen release capacity of oxygen carriers.

5. Other Catalytic Removal Methods

In a CFB boiler, the bed material interacts with N₂O in flue gas in the furnace and gassolid separator. These bed materials, composed of various metal oxides, can catalyze the destruction of N₂O, so as to accelerate the decomposition reaction. Circulating ash usually has a narrower particle size distribution, larger specific surface area and less carbon content than the bed material and may be an excellent catalyst to accelerate N₂O decomposition. Hou et al. [93] studied the catalytic decomposition of N₂O by circulating ash in a coal-fired circulating fluidized bed boiler. The results showed that different metal oxides had different catalytic decomposition effects on N₂O. CaO and Fe₃O₄ were very active, while Al₂O₃ and SiO₂ had little destructive effect on N₂O. It was found that even if the oxygen content was very small, it worsened the catalytic decomposition of N₂O.

6. Conclusions

 N_2O is a non-negligible pollutant in CFB. This paper reviews the catalytic removal technology of N_2O and summarizes the latest research progress in catalytic decomposition methods such as noble metals, metal oxides and molecular sieves. The main conclusions are as follows:

- Noble metals show good N₂O decomposition performance at low temperatures, but they have high costs, a narrow temperature window and can easily lead to poisoning by oxygen and water vapor.
- 2. A metal-ion-modified molecular sieve has higher activity and better low-temperature activity, but its hydrothermal stability is poor.
- Metal oxides have high thermal stability, so they are more suitable for use in CFB. Among them, hexaaluminate oxide has a large high-temperature specific surface area, excellent sintering resistance and thermal shock resistance and has high removal efficiency and selectivity for N₂O. It is a very promising high-temperature N₂O decomposition catalyst.
- 4. Partial or total replacement of silica sand with an oxygen carrier may help to promote oxygen distribution in the combustion chamber, which is called OCAC. OCAC can significantly reduce the concentrations of carbon monoxide and nitric oxide in the furnace. Therefore, it can also be considered to reduce N₂O emissions in CFB boilers.

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