

Chapter 2

Status of Coal Gas H₂S Removal

2.1 Clean Coal Technology

Coal is found in huge amounts throughout the world and has lower cost as compared to other fossil fuels [1], it represents at present about 70% of the world's proven fossil fuel resources; therefore, coal is probably to remain one of the most important sources of primary energy for a long time, playing a strategic role in the medium–long-term energy production systems. However, coal utilization has a few negative impacts on the environment and atmosphere; the critical issue in promoting coal utilization is environmental pollution control without reducing the energy efficiency. Coal is a complex chemical mixture composed of carbon, hydrogen, and dozens of trace elements. When coal is severed as a fuel source, some of these elements would convert to gaseous emissions, such as sulfur dioxide (SO₂) or hydrogen sulfide (H₂S), nitrogen oxides (NO_x), mercury, and other chemical by-products via the coal combustion or thermal decomposition. These emissions have been established to possess detrimental effects on the environment and human health, which contributes to acid rain, lung cancer, and cardiovascular disease [2, 3].

Thus, clean coal technologies are needed to utilize coal in an environmentally acceptable way and to improve coal utilization efficiency. Clean coal technology is a collection of new technologies for coal processing, coal combustion, coal conversion, as well as pollutant emission control which are developed to attempt to mitigate the environmental pollution and increase the energy efficiency during coal development and application procedures. The traditional clean coal technologies mainly consist of coal washing, coal blending, coal modeling, and fine coal ash utilization technologies. Nowadays, clean coal technologies are grouped into three categories: pre-combustion technologies (coal processing and conversion), in-combustion technologies (combustion adjusting and optimization), and post-combustion technologies (flue gas clean). Concerns on clean coal technologies exist in regarding the economic viability of these technologies and the timeframe of

delivery, potentially high hidden economic costs in terms of social and environmental damage, and the costs and viability of disposing of removed carbon and other toxic matter.

2.1.1 Pre-combustion Clean Technologies

In recent years, coal conversion (coal gasification or liquefaction) has been regarded as one of the most promising coal clean technologies, because most of the hazardous components, such as sulfur and mercury, can be captured or removed by means of coal gasification or liquefaction prior its application for power generation. Coal gasification is a process of producing syngas (a gas mixture primarily consisting of carbon monoxide (CO), hydrogen (H₂), carbon dioxide (CO₂), methane (CH₄), and water vapor (H₂O) from coal and water) at high temperature (>1000 °C) which uses air and/or oxygen as the gasifier. Historically, coal was gasified using early technology to produce coal gas (also known as “town gas”) which is employed for municipal lighting and heating before the advent of industrial-scale production of natural gas. In current practice, large-scale instances of coal gasification are primarily applied for electricity generation, such as in integrated gasification combined cycle (IGCC) power plants. Alternatively, coal-derived syngas can be converted into transportation fuels such as gasoline and diesel through additional treatment via the Fischer–Tropsch process or into methanol which itself can be used as transportation fuel or fuel additive, or which can be converted into gasoline by the methanol to gasoline process. During gasification, the sulfur element and mercury element will be released mainly in the form of hydrogen sulfide and elemental mercury, respectively, which can be captured or removed by solid sorbents, then the clean syngas would be charged to gas turbines or combustors for power generation, which is the so-called pre-combustion clean technology, from which carbon dioxide can also be efficiently captured and separated, transported, and ultimately sequestered.

Coal liquefaction is a process of converting coal into value-added liquid hydrocarbons: liquid fuels and petrochemicals, which is commonly referred to “Coal to Liquid Fuels” (CTL) in industry, although “liquefaction” is generally used for a non-chemical process of becoming liquid. Specific liquefaction technologies generally fall into two categories: direct (DCL) and indirect liquefaction (ICL) processes. Indirect liquefaction processes generally involve the first gasification of coal to syngas and then converting the syngas into liquid hydrocarbon by using a process such as Fischer–Tropsch process. On the contrary, direct liquefaction processes convert coal into liquids directly, without the intermediate step of gasification, by breaking down its organic structure with application of solvents or catalysts in a high-pressure and temperature environment. Since liquid hydrocarbons generally have a higher hydrogen/carbon molar ratio than that of coal, either hydrogenation or carbon-rejection process must be employed in both ICL and DCL technologies. However, as the coal liquefaction usually is a high-temperature or

high-pressure process, they require a significant energy consumption and, at industrial scales (thousands of barrels per day), multibillion-dollar capital investments. Thus, coal liquefaction is only economically viable at historically high oil prices and therefore presents a high investment risk.

2.1.2 Combustion Adjusting and Optimization

Adjusting and optimizing the coal combustion procedure is also considered as an effective coal clean technology, which mainly including oxy-fuel combustion, fluidized bed combustion, and supercritical and ultra-supercritical systems. Oxy-fuel combustion, a process of burning a fuel using pure oxygen instead of air as the primary oxidant, is often combined with staged combustion for nitrogen oxide reduction because pure oxygen can stabilize combustion characteristics of a flame. Since the nitrogen component of air is not heated, lower nitrogen oxides and higher flame temperatures are possible. However, firing with pure oxygen would result in a too high flame temperature, so oxygen is usually diluted by blending with recycled flue gas, or staged combustion (staged combustion is a process that coal at first combusts without oxygen, in which the nitrogen elements in coal would transform into nitrogen (N_2), then oxygen is injected into the boiler to make coal completely combust, which can reduce the nitrogen oxide (NO_x) emissions by about 30–40%). The recycled flue gas can also be used to carry fuel into the boiler and ensure adequate convective heat transfer to all boiler areas. Oxy-fuel combustion has significant advantages over traditional air-fuel combustion. First, less heat is lost in the flue gas as oxy-fuel combustion produces approximately 75% less flue gas than that of air-fuel combustion, the exhaust of oxy-fuel combustion process primarily consists of carbon dioxide and water which are suitable for sequestration. Most of the flue gases are condensable; this makes compression separation possible. Second, since nitrogen from air is absent, nitrogen oxide production can be greatly reduced. The main problem for oxy-fuel combustion is separating oxygen from air, this process needs lots of energy, nearly 15% of production by a coal-fired power station can be consumed for this process. Economically speaking, oxy-fired plants cost more than traditional air-fired plants [4]. However, a new technology which is not yet practical called chemical looping combustion can be used to reduce this cost. At present in the absence of any need to reduce CO_2 emissions, oxy-fuel combustion is not competitive.

Fluidization is the phenomenon by which solid particles are transported into a fluid-like state through suspension in a gas or liquid. The fluidized bed combustion process can facilitate electricity generation for power plants via firing a wide range of fuels (coal or biomass) while meeting the stringent pollutant emission requirements as well. The fuel burning for fluidized bed usually occurs at 760–930 °C, well below the 1370 °C needed to generate nitrogen oxide pollutants, which basically permits the possibility of a strong reduction of sulfur dioxide and nitrogen oxide emissions with respect to the pulverized-coal power plants. Sulfur dioxides

are removed by limestone injection and carbon dioxides are captured by solid sorbents, then the purified flue gas can be charged into gas turbines. Fluidized bed combustion technologies are of various types which mainly include atmospheric pressure fluidized bed combustion (FBC), circulating fluidized bed combustion (CFBC) or pressurized fluidized bed combustion (PFBC), and pressurized circulating fluidized bed combustion (P-CFBC). Supercritical fluid is any substance at a temperature and pressure above its critical point, where distinct liquid and gas phases do not exist, it can effuse through solids like a gas, and dissolve materials like a liquid. In addition, close to the critical point, small changes in pressure or temperature result in large changes in density, allowing many properties of a supercritical fluid to be “fine-tuned.” Supercritical fluids are suitable as a substitute for organic solvents in a range of industrial and laboratory processes. Carbon dioxide and water are the most commonly used supercritical fluids, being used for decaffeination and power generation, respectively. As we know, the efficiency of a heat engine is ultimately dependent on the temperature difference between heat sources and sinks (Carnot cycle). To improve the efficiency of power stations, the operating temperature must be raised. If we use water as the working fluid, the system efficiency can be increased from about 39% for current technology to about 45% for subcritical operation. A supercritical steam generator is a type of boiler that operates at supercritical pressure, frequently used in the production of electric power. In contrast to a subcritical boiler in which bubbles can form, a supercritical steam generator operates at pressures above the critical pressure of 22 MPa. Therefore, liquid water immediately becomes steam. Water passes below the critical point as it does work in a high-pressure turbine and enters the generator’s condenser, resulting in slightly less fuel use and therefore less greenhouse gas production. The currently available power plants based on supercritical steam boiler at 600 °C permit efficiency of 45–74% [5].

2.1.3 Flue Gas Emission Controls

In practice, post-combustion technologies or flue gas emission controls are the most extensively used clean technology for coal-fired power plants. Flue gas is the gas mixture exiting to the atmosphere via a flue which is a pipe or channel for conveying exhaust gases from a fireplace, oven, furnace, boiler, or steam generator. Generally, the flue gas refers to the combustion exhaust gas produced at power plants, though its composition depends on which kind of fuel is being burned, it usually consists of mostly nitrogen (typically more than two-thirds) derived from the combustion of air, carbon dioxide, and water vapor as well as excess oxygen (also derived from the combustion air). It further contains a small percentage of various pollutants, such as particulate matter (like soot), carbon monoxide, nitrogen oxides, and sulfur oxides. Since the combustion pollutants possess significantly detrimental effects on the environmental and human beings, which contribute to the formation of smog and acid rain as well as tropospheric ozone. There are many

proven technologies for removing pollutants emitted from power plants that are now available, such as flue-gas desulfurization (FGD), selective catalytic reaction (SCR) as well as carbon capture and storage (CCS).

At power plants, flue gas is often treated with a series of chemical processes and scrubbers which are employed for remove pollutants. Electrostatic precipitators (ESP, a filtration device that removes fine particles, like dust and smoke, from a flowing gas using the force of an induced electrostatic charge minimally impeding the flow of gases through the unit) or fabric filters are applied for capturing particulate matters, and FGD captures the sulfur dioxide produced by burning fossil fuels, particularly coal. Nitrogen oxides are treated either by mid-temperature SCR with ammonia or urea of which aim is to produce nitrogen gas rather than nitrogen oxides. In the USA, nowadays, there is a rapid development of technologies to remove mercury from flue gas, typically by absorption on sorbents or by capture in inert solids as part of the flue-gas desulfurization product. FGD is a set of technologies used to remove sulfur dioxide from exhaust flue gases of fossil-fuel power plants and from the emissions of other sulfur oxide emitting processes. The commonly applied methods for FGD mainly consist of wet scrubbing and dry injection technologies. Wet scrubbing technology uses a slurry of alkaline sorbents, usually limestone, lime, or seawater to scrub acid gases; while dry injection technology sprays similar sorbent slurries into the desulfurization tower to adsorb acid gases. In wet scrubbing systems, the flue gas first passes through a fly ash removal device, either an electrostatic precipitator or a baghouse, and then into the SO_2 absorber. However, in dry injection or spray drying operations, SO_2 is first reacted with the sorbent, and then the flue gas passes through a particulate control device. Most FGD systems employ two stages: one for fly ash removal and the other for SO_2 removal. Attempts have been made to remove both the fly ash and SO_2 in one scrubbing vessel. However, these systems experienced severe maintenance problems and low removal efficiency.

SCR is a means of converting NO_x with the aid of a catalyst into diatomic nitrogen (N_2) and water (H_2O). A gaseous reductant, typically anhydrous ammonia, aqueous ammonia, or urea, is added to the stream of flue or exhaust gas and is adsorbed onto a catalyst. CO_2 is also a reaction product when urea is used as the reductant. In power stations, the same basic technology is employed for removal of NO_x from the flue gas of boilers used in power generation and industry. In general, the SCR unit is located between the furnace economizer and the air heater, the ammonia is injected into the catalyst chamber through an ammonia injection grid. Operation temperature usually plays a critical role in SCR applications. Ammonia slip is also a key issue for SCR technology application in power plants. Other issues that must be considered in using SCR for NO_x emission control in power plants are the formation of ammonium sulfate and ammonium bisulfate attributed to the sulfur content in the fuel as well as the undesirable catalyst-caused formation of SO_3 from the reaction of SO_2 and O_2 in the flue gas. SCR catalysts are grouped into two categories: unsupported and supported catalysts. Unsupported catalysts are made of pure base metal catalysts, such as vanadium and tungsten, which are lack of high thermal durability but are less expensive and operate very well in the temperature ranges most commonly seen in industrial and utility boiler applications. Supported

catalysts are composed of active catalytic components as well as carriers, the active components usually are made of base metals (such as vanadium, molybdenum, and tungsten), and titanium oxide is often used as carriers, activated carbon is also developed as the catalyst support which is applicable for NO_x removal at low temperatures. In addition, zeolite catalysts have the potential to operate at substantially higher temperature than base metal catalysts, they can withstand prolonged operation at 900 K and transient conditions of up to 1120 K. Zeolites also possess a lower potential for potentially damaging SO₂ oxidation. Iron- and copper-exchanged zeolite urea-SCR has been developed with approximately equal performance to that of vanadium urea-SCR when the fraction of NO₂ is 20–50% of the total NO_x. The two most common designs of SCR catalyst geometry used today are honeycomb and plate. The honeycomb form usually is an extruded ceramic applied homogeneously throughout the ceramic carrier or coated on the substrate. Plate-type catalysts have lower pressure drops and are less susceptible to plugging and fouling than the honeycomb types, but plate configurations are much larger and more expensive. Honeycomb configurations are smaller than plate types, but have higher pressure drops and plug much more easily. A third type is corrugated, comprising only about 10% of the market in power plant applications.

CCS is the process of capturing waste carbon dioxide from large point sources, such as fossil fuel power plants, transporting it to a storage site, and depositing it where it will not enter the atmosphere anymore, normally an underground geological formation. The aim is to prevent the release of large quantities of CO₂ into the atmosphere, which is a potential means of mitigating the contribution of fossil fuel emissions to global warming and ocean acidification. Although CO₂ has been envisaged either in deep geological formations or in the form of mineral carbonates for several decades for various purposes, including enhanced oil recovery, the long-term storage of CO₂ is a relatively new concept. CO₂ can be captured out of air or fossil fuel power plant flue gas using adsorption (or carbon scrubbing), membrane gas separation, or adsorption technologies. Amines are the leading carbon scrubbing technology. Capturing and compressing CO₂ may increase the energy needs of a coal-fired CCS plant by 25–40%. These and other system costs are estimated to increase the cost per watt energy produced by 21–91% for fossil fuel power plants. Applying the technology to existing plants would be more expensive, especially if they are far from a sequestration site. Technologies based on regenerative capture by amines for the removal of CO₂ from flue gas have been deployed to provide high purity CO₂ gas to the food industry and for enhanced oil recovery. They are now under active research as a method for CO₂ capture for long-term storage as a means of greenhouse gas remediation and have begun to be implemented in a limited way.

2.2 H₂S Removal for Integrated Gasification Combined Cycle

2.2.1 Introduction of Integrated Gasification Combined Cycle

China is a country which is rich in coal resources but poor in petroleum and gas. Based on the BP statistical review of China energy of 2016, Coal still accounts for 64% of the primary energy consumption, thus it is the most important primary energy. Most of the coal is used for electric power generation; however, the thermal efficiency and electricity supply efficiency of the conventional coal-fired power generation technology are too low, and the exhaust (SO₂, NO_x, trace elements) emitted from the coal-fired power plants can cause severe environmental problems, such as greenhouse effect and air pollution. In recent years, haze has become a serious issue in many Chinese big cities, which is detrimental to the individual healthy and has a negative influence on the development of the Chinese economy. Therefore, clean coal technology is highly important for the sustainable development of the Chinese environment and economy [6–8].

Integrated gasification combined cycle (IGCC) power technology has been regarded as one of the most promising clean coal technologies in the twenty-first century attributed to its environmental friendliness, economic efficiency, and thermal efficiency. The schematic of the IGCC system is depicted in Fig. 2.1, the coarse coal gas is generated at high temperature (800–900 °C) from the gasifier, it is firstly cooled down by a cooler and purified with a dust collector to get rid of the dust particles and alkali metals, and then goes to the desulfurizer to remove the

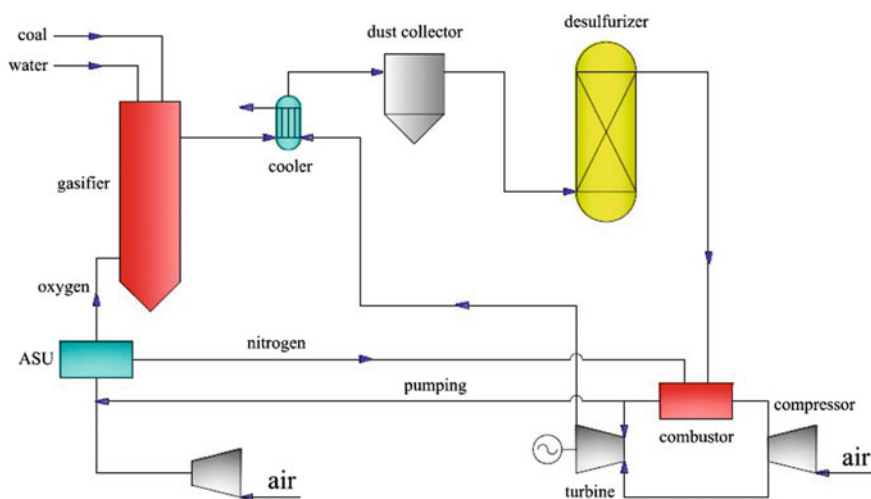


Fig. 2.1 Schematic diagram of IGCC power technology

sulfur components (H₂S, COS, CS₂), eventually, the clean coal gas is charged into the combustion chamber of the gas turbine for combustion with air, the generated high-temperature flue gases are then pressured into the turbine for electricity power generation, in which part of the air of high-pressure derived from the compressor of the combustion chamber will go to the air separation units (ASU) to separate oxygen for the gasifier, all the nitrogen obtained from the ASU is charged into the combustion chamber of the gas turbine to control the temperature [9].

2.2.2 Integrated Gasification Combined Cycle Desulfurization

In IGCC system, the syngas after purification produced via high-temperature coal gasification in the gasifier is used as fuel for the gas turbine for electric power generation, and the steam produced by the syngas coolers in the gasification section is also used by the steam turbine for electric power generation, in this way, the gas turbine and the steam turbine work together well combining the high-temperature heat input process and the low-temperature heat output procedure, which can significantly increase the system thermal efficiency to as high as 43–45% [10]. However, the coarse coal gas derived from coal gasification process usually contains large amounts of H₂S, COS, CS₂ (90% of them is H₂S) as well as HCl, HCN, NO_x and alkali metals which can cause severe corrosion of gas turbine leaves and reduce its serving lifetime. The exhaust is also harmful to the environment.

The operation temperature of the gasification process is usually above 1000 °C; the temperature of its outlet gas (coarse coal gas) is between 800 and 900 °C [11]. The conventional desulfurization approach is wet absorption technique which can only occur at a much lower temperature than the gasification temperature. The hot coarse coal gas is first cooled down to 40–50 °C and adsorbed by amine scrubbers using organic or inorganic solution as solvents and then reheated up before going to gas turbines, which results in substantial heat loss due to the syngas cooling down and the subsequent reheating up process. Besides, oxygen is the commonly used gasifier in recent years, and the ASU also consumes a lot of electricity, both could reduce the overall thermal and economic efficiency of the IGCC system. The desulfurization by using regenerable solid sorbents at high temperature, which does not need the syngas cooling down and the subsequent reheating up process, can not only improve the system thermal efficiency but also simplify the purification equipment. Therefore, how to effectively remove the pollutants in the coarse coal gas at high temperature and develop efficient, stable, and regenerable high-temperature desulfurizers have become a key part in clean coal technology [12, 13].

2.3 Low-Temperature Coal Gas Desulfurizers

The unwanted by-products of sulfur-containing compounds (H_2S and COS), commonly existed in the biogas produced from the gasification of biomass feedstocks and the hot coal gas derived from coal gasification processes, need to be removed prior to syngas application because of their corrosive effects on the gas transmission and distribution system as well as their detrimental influences on the catalyst performance, such as tar reforming catalysts [14, 15], Fischer–Tropsch synthesis catalysts [16], and air pollutant oxidation catalysts [17–19]. The required sulfur concentrations by downstream processes are below 0.1 parts per million by volume (ppm) for proton membrane exchange (PEM FC) fuel cell and below 20 ppm for IGCC system. Besides, desulfurizers must have acceptable sulfur capacity in terms of both theoretical values and achievable ranges, preferably be regenerable, and maintain activity and capacity during many sulfidation/regeneration cycles [20]. The desulfurizers should also be nonpyrophoric for fuel cell applications, and finally must be economically acceptable. Few studies had been devoted to the development of the sorbents for hydrogen sulfide removal below 400 °C, which is the so-called low-temperature desulfurizer, because its sulfidation temperature is much lower than those (600–850 °C) extensively applied for hot coal gas cleanup. There are a couple of applications in which an extremely low (<1 ppm) sulfur concentration is required, including ammonia synthesis, water-gas shift process, PEM fuel cells using hydrogen-rich gas as the feed, and pure hydrogen for applications [21, 22].

Westmoreland and Harrison [23] and Hepworth et al. [24] performed the thermodynamic calculation studies of the reactions between hydrogen sulfide and different metal oxides, which are divided into two groups with respect to the reaction temperatures: one is high-temperature (>600 °C) sorbents such as Ba, Ca, Sr, Cu, Mn, Mo, W; another is low-temperature (300–550 °C) sorbents such as V, Zn, Co, Fe. Among them, ZnO shows the highest sulfidation equilibrium constant at low-temperature range, which yields H_2S lowering down to even 1 ppm corresponding to the complete conversion of ZnO to ZnS. Rosso and coauthors [25] prepared several pure ZnO sorbents by using combustion synthesis and a modified citrate method for syngas desulfurization at 250 °C, the ZnO sorbents obtained from calcination at the lowest temperatures and with the consequent highest specific surface area and pore volume presented the highest sulfur trapping capacity, it can only be partially recovered by regeneration conducted for 15 min at 625 °C in air because of an unavoidable progressive sintering. The hydrogen sulfide capture from steam-containing gas mixtures over ZnO-based sorbents at low temperature for fuel cell applications was conducted by Novochinskii and coauthors [26, 27], sorbent formulation and preparation techniques had great influences on the sulfidation performance, ZnO-based sorbent can effectively capture H_2S from reformat and provide an extremely low outlet H_2S concentration (<20 ppb). Its sulfur-capturing capacity increased with decreasing temperature of the feed gas, the increase in steam concentration decreased the H_2S capture and caused the release of previously

captured H₂S, greater inlet H₂S concentrations and lesser space velocities improved the sulfur-capturing capacity of ZnO; however, carbon dioxide had a negative impact on the sulfur capacity. Wang and coauthors [28] supported ZnO nanoparticles onto SBA-15 via incipient wetness impregnation and ultrasonic approach followed by in situ activation at 523 K; the as-obtained sorbents exhibited a superior ability in lowering hydrogen sulfide down to parts per billion (ppb) from gas stream at room temperature, and the highest breakthrough sulfur capacity of 43.6 g S/100 g was achieved for 3.04 wt% ZnO/SBA-15 due to the integration of the high surface area mesoporous SBA-15 and the promising sulfidation properties of ZnO nanoparticles. They also synthesized aluminum mesoporous silicate (Al-SBA-15)-supported ZnO nanoparticles by post-synthesis and immobilization method via microwave-assisted route [29], the as-synthesized sorbents had well-ordered hexagonal mesopores and were abundant in micropores, ZnO nanoparticles dispersed well and anchored both in the channel and the wall of mesoporous silica, 2.1 wt% ZnO/Al-SBA-15 exhibited the highest H₂S uptake capacity at ambient temperature, both micropores and mesopores are active sites for H₂S capture, especially micropores, the enhancement of sulfur capacity was attributed to the integration of the pore structures of mesoporous silica as well as the attractive sulfidation properties of ZnO nanoparticles. Skrzypski and coauthors [30] synthesized pure and metal-doped ZnO nanostructure sorbents by using coprecipitation method to clarify the impacts of metals (Fe, Co, Ni, Cu) on the transformation kinetics at 200–350 °C, during sulfidation of Cu-doped ZnO the gas diffusion was faster than for all other metal-doped ZnO, there was no correlation between the sulfidation rate and the textural properties of formed sulfides, indicating that sulfur transport during sulfidation occurred by solid state rather than gas phase diffusion, Cu₂S–ZnS solid solution was formed during sulfidation of the Cu-doped ZnO, which infers that the diffusion enhancement in the addition of copper was brought about by sulfur vacancies created through charge compensation of Cu⁺ replacing Zn²⁺. Wang and coauthors [31] developed series of novel zinc oxide–silica composites with three-dimensionally ordered macropores (3DOM) structure via colloidal crystal template method at the first time and applied for hydrogen sulfide removal at room temperature, the sorbent with 3DOM structures showed remarkable desulfurization performance at room temperature attributed to the unique structural features of 3DOM composites, high surface areas, nanocrystalline ZnO and the well-ordered interconnected macroporous with abundant mesopores. The introduction of silica was beneficial to support the 3DOM structure and the high dispersion of ZnO, the multiple adsorption/regeneration cycles showed that the 3DOM ZnO–SiO₂ composite was stable and its sulfur capacity could still reach 67.4% of that of the fresh one at the fifth cycle.

Iron oxide also showed potential ability for hydrogen sulfide removal at low temperatures, Sahu and coauthors [32] made an iron-based sorbent by using red mud which is a caustic waste product of alumina industry, it performed effectively for hydrogen sulfide removal at ambient conditions, XRD and EDX data confirmed that hydrogen sulfide was captured in the form of FeS₂, FeS, CaSO₄·2H₂O, sulfur, sulfide, and bisulfide of Na. Long and Loc [33] reported a low-cost extruded

iron-based sorbent containing Fe_2O_3 and bentonite prepared by using hydrothermal-precipitation method for hydrogen sulfide cleanup at room temperature, the total H_2S uptake slightly increased with increasing bed depth and initial H_2S concentration, and decreased with incremental flow rate. Pahalagedara and coauthors [34] developed mesoporous cobalt oxides with tunable porosity and crystallinity by using an inverse micelle soft template method and employed for desulfurization at temperature of 25–250 °C, a considerably high sulfur sorption capacity of 13.4 g S/100 g was reached even at room temperature, and very high values of 65.0–68.9 g S/100 g were achieved in 175–250 °C temperature range, the presence of surface exposed particles and interconnected intraparticle voids was regarded as the critical factors for the H_2S diffusion ability, other mesoporous metal oxides (Cr_2O_3 , CuO , Mn_2O_3 , and Fe_2O_3) synthesized by the same method also showed sulfur capacities of 2–200 times more than that of their corresponding nonporous ones.

Apart from the metal oxides, porous carbon and zeolite materials obtained from industrial wastes have also been investigated for desulfurization. Primavera and coauthors [35] employed activated carbon as a catalyst for oxidation of hydrogen sulfide (1–3%) to elemental sulfur from tail gases originating from geothermal plants, the exist of water has a beneficial influence on the catalytic performance, particularly, it enhances the reaction rate and the amount of sulfur that can be loaded before regeneration. Adib and coauthors [36] analyzed the relationship between sulfur capacities and surface properties of unimpregnated activated carbons, they found that the potential of unimpregnated carbon serving as hydrogen sulfide sorbent highly depended on its acidity such as numbers of acidic groups, pH values, amounts of surface oxygen groups, or weight loss associated with the decomposition of surface oxygen species, there are certain threshold values of these quantities which, when exceeded, would significantly affect the breakthrough sulfur capacity. Bagreev and coauthors [37] made an activated carbon sorbents derived from sewage sludges for hydrogen sulfide removal from moist air; the sorbents prepared by carbonization at 950 °C has a sulfur capacity twice of that of coconut shell-based activated carbon, the sulfur capacity of the sewage sludge-derived sorbents increase with the elevation of the carbonization temperature, they were efficient for hydrogen sulfide removal until the pore entrances are blocked with product sulfur, and chemisorption plays an important role in hydrogen sulfide removal from moist air over activated carbon. Kastner and coauthors [38] reported that wood and coal fly ash were used as inexpensive catalysts for catalytic oxidation of hydrogen sulfide to elemental sulfur at low temperatures of 23–25 °C, wood ash (44.9 m^2/g) had a much higher surface area than that of coal ash (7.7 m^2/g), leading to a higher initial H_2S removal rate, activity deactivation occurred because of the surface deposition of sulfur and a subsequent decline in surface area, the carbon-based catalysts can be regenerated by using hot water of 85 °C. Three sewage sludges collected at wastewater treatment plants by Ros and coauthors [39] were employed as precursors of sorbents or catalysts for H_2S removal at room temperature. Thermal treatment (gasification) of the raw (dried) sludges can increase the H_2S removal ability, catalytic oxidation of hydrogen sulfide to

elemental sulfur and sulfate moieties was the main route of H₂S removal, sorbent obtained from an iron/calcium-containing sludge was the most reactive one with the highest capacities for H₂S retention, alternatively, the oxidation ability of H₂S by using chars obtained from the other two sludges was related to their textural properties. Xu and coauthors [40] developed a novel nanoporous sorbent via loading polyethylenimine (PEI) into the mesoporous molecular sieve MCM-41 for effectively adsorbing H₂S from gas mixture at low temperature, the performance of the new sorbent was better than that of a commercial ZnO, its sulfur capacity was relatively low, which may be further improved by other synthesis techniques. Rezaei and coauthors [41] studied the sulfur capacities of titanasilicate-supported copper sorbents, copper supported on Engelhard Titanasilicate-2 was a superior H₂S scavenger for maintaining H₂S levels below 0.5 ppm due to its high cation exchange capacity and copper dispersion, and it showed higher utilization at room temperature when compared to commercial sorbents, the nonporous nature of Engelhard Titanasilicate-2 structure takes advantage of the ion exchange features of microporous frameworks.

2.4 High-Temperature Coal Gas Desulfurizers

Solid sorbents (single metal oxides or metal oxide composites) are usually used for hydrogen sulfide removal from hot coal gas derived from coal gasification, which is the so-called dry adsorption desulfurization.

2.4.1 *Unsupported Desulfurizers*

(1) **Transition Metal Oxides**

Transition metal oxides are considered as the first generation high-temperature desulfurizers, Elseviers and Verelst [42] carried out the thermodynamic equilibrium simulations of various metal oxides to determine suitable materials for intensive desulfurization of fuel gases from the IGCC system, they found that zinc-based materials are the most promising for high temperature intensive desulfurization; however, zinc-based materials can cause evaporation and regenerability problems. In 2000, Slimane and Abbasian [43, 44] from the Institute of Gas Technology (IGT) conducted a systematical research on the sulfidation performance and regenerability of the iron-, copper-, zinc-, and manganese-based sorbents in a fluidized-bed reactor in temperature range of 350–550 °C, copper-based sorbent possessed the best combination of high attrition resistance and sulfidation reactivity, sulfur-removal efficiency, and pre-breakthrough conversion, manganese-based sorbent also showed an encouraging results but it needs a high regeneration temperature of 550 °C; however, iron-based sorbent did not show sufficient sulfidation

reactivity in the moderate temperature range. However, they found that the low-cost iron oxide waste materials from metal processing operations and one coal bottom ash were the most reactive toward hydrogen sulfide removal in temperature range of 400–600 °C and presented the highest effective sulfur capacity. Kobayashi and co-workers [45, 46] performed a series of reduction and sulfidation tests of zinc ferrite-silica composite powders at mainly 450 °C in a simulated coal gas environment, they reported that ZnS and FeS were produced at 1 vol.% H₂S, whereas zinc sulfides were the sole sulfidation product at 80 ppm H₂S; the breakthrough time strongly depends on the changes in zinc sulfur capacity which might level off at around 40% of its initial value within 50 cycles. Bu and coauthors [47, 48] developed several zinc-based sorbents for hot gas desulfurization at temperature of 450–800 °C in a gas mixture consisting of 1.0–1.4% H₂S, 20% H₂, 15% H₂O balanced with nitrogen and regenerated by using 3–6% O₂/N₂ mixture at 650–700 °C, the zinc-based sorbents were named as G-201, G-202, L-991, and L-992, respectively; G-201 and G-202 could reduce H₂S from about 10 g/m³ to less than 20 mg/m³, and the sulfur capacities both increased with temperature rising, no decrease in sulfur capacity of G-201 (19.43–24.23 g/100 g) occurred during 20 desulfurization/regeneration cycle tests, no occurrence of striping, attrition, and sintering on the surface of used sorbents was found after the longtime test, the reactivity was stable with a sulfur capacity of 21.19 g/100 g after 1500 h test, the hydrogen sulfide concentration can also be reduced by L-991 and L-992 from about 10 g/m³ to less than 20 g/m³ with sulfur-removal efficiency >99%.

Though ZnO has a high sulfur adsorption capacity, reduction of ZnO in highly reducing atmosphere of syngas followed by vaporization of elemental zinc above 600 °C can present a significant sorbent loss [49]. Iron oxide is the most commonly used sorbents for hot coal gas desulfurization due to economic consideration and its favorable dynamic property. Pan and coauthors [50] made a special sorbent containing Fe₂O₃·FeO (particle sizes are in the range of 0.042–0.12 mm) which is more attractive for both sulfidation and regeneration stages as compared to zinc-based sorbents, its sulfidation capacity sharply increases with temperature in the range of 500–600 °C and reached its maximum absorption capacity at 600 °C, its sulfidation capacity is 1.9 times higher than that of zinc titanate. In recent years, the high-temperature desulfurization of iron oxide has been extensively studied by the Institute for Chemical Engineering of Coal at Taiyuan University of Technology [51], including the effects of the synthesis methods, phase structures, textural properties (surface area, pore diameter and pore volume), as well as sulfidation conditions on the desulfurization performance of the iron oxide, its sulfidation-regeneration behavior and kinetics have also been studied. Fan and co-workers [52] found that the addition of calcium oxide additive benefited the utilization of iron oxide sorbent in strongly reducing atmospheres, the reduction temperature of the sorbent increased with the increasing content of calcium which plays a role of retarding the reduction reaction; calcium participated in every sulfidation/regeneration cycle, the calcium sulfate formed during desulfurization process was decomposed and regenerated to CaO by reacting with CO before the next sulfidation process, which contributes to the enhancement of sulfur capacity.

Zhu and co-workers [53] prepared six iron-based sorbents with binders of different argillaceous minerals by mechanically mixing to alleviate the sorbent pulverization in IGCC hot coal gas desulfurization, NTKW2 sorbent with binder of clay had a better sulfidation performance, and it had a more stable performance with the best desulfurization efficiency and mechanical strength, its optimal reaction temperature was 550 °C. To better understand the sulfidation behavior and mechanism of iron-based sorbents, Ren and coauthors [54] investigated intrinsic sulfidation behavior of Fe₂O₃ in H₂S/N₂ gas mixture for the sake of improving its desulfurization performance; they revealed that the intrinsic H₂S removal by Fe₂O₃ would produce multi-phase of sulfides. Wang and coauthors [55] studied the effects of Mo addition on the sulfidation behavior of iron oxide-based sorbents at temperature between 400 and 600 °C, the results show that doping Mo into iron oxides may effectively improve the desulfurization efficiency and increase the compressive strength of iron-based sorbents. Fan and co-workers [56] synthesized a novel iron oxide sorbents with three-dimensionally ordered macropores (3DOM) structures ranging in size from 60 to 550 nm, and they are creatively used as sorbents for H₂S removal at temperatures of 300–350 °C, the 3DOM iron oxide sorbent shows much higher reactivity and efficiency with respect to the iron oxide synthesized by using conventional mixing method, the excellent sulfidation performance of 3DOM iron oxide is attributed to its special texture, such as the open and interconnected macroporous, large surface area, and Fe₂O₃ nanoparticle.

Copper-based sorbents have also been extensively employed for high-temperature desulfurization owing to the favorable thermodynamic equilibrium between copper oxides and hydrogen sulfide, CuO can reach low levels of H₂S in clean fuel gas if the CuO is not reduced to elemental Cu. Patrick and Gavalas [57] studied the sulfidation/regeneration behavior of CuO/Al₂O₃ sorbents at temperature range of 550–800 °C in a gas mixture of H₂S, H₂, H₂O balanced with N₂, they disclosed that alumina stabilized CuO against complete reduction to Cu, the low pre-breakthrough H₂S levels were assigned to the sulfidation of copper oxide at oxidation states of +1 or +2, the sulfided sorbents were completely regenerable in air/N₂ mixtures. Li and Flytzani-Stephanopoulos [58] synthesized two binary CuO–Cr₂O₃ and CuO–CeO₂ sorbents by using citrate method for high-temperature fuel gas desulfurization, they both can reduce H₂S from simulated coal-derived fuel gas to less than 5–10 ppm at temperature of 650–850 °C, the presence of stable CuCr₂O₄ in CuO–Cr₂O₃ sorbent retains some copper in Cu²⁺ or Cu⁺ oxidation states, which contributes to the high sulfur-removal efficiency; however, CeO₂ in CuO–CeO₂ sorbent had little influence on stabilizing CuO against reduction to Cu. Abbasian and Slimane [59] developed a regenerable copper chromite sorbent with superior hot fuel gas desulfurization performance for IGCC applications at temperature of 550–650 °C, it can achieve less than 5 ppm H₂S concentration despite its considerably high crush strength; in terms of sulfur-removal efficiency and effective capacity, the optimum desulfurization of the copper chromite sorbent temperature is about 600 °C, it can be regenerated with dilute O₂/N₂ gas mixtures at 750 °C. However, CuO is also readily reduced to metallic Cu in a high temperature and strongly reducing atmosphere and elemental

Cu is an order of magnitude less active in high-temperature desulfurization than Cu_2O and CuO , doping other metal oxides into CuO is a good way to stabilize CuO . Wang and co-workers [60] developed new kinds of calcium-based sorbents (Ca–Al–O regenerable sorbents with various calcium contents) by co-precipitation method for H_2S removal at 850°C , the sulfur capacity of the sorbent with 52.5 wt % CaO content reached 36 g S/100 g; however, the spent sorbent cannot be completely regenerated by diluted air due to the formation of CaSO_4 , which inhibits oxygen diffusion and slows or even stops the regeneration reaction. Four-time oxidation/reduction cycles can completely regenerate the sorbent, when the sorbents were alternately and repeatedly subjected to oxidation and reduction, CaS first converted to calcium sulfate and then to calcium oxide. Oxidation with 3% O_2 in diluted air and reduction with 10% H_2 can regenerate the sorbent for subsequent sulfidation cycles, while higher O_2 concentration may reduce the sulfur capacity because of heat-induced sintering. The spent sorbent can also be regenerated well by steam, in which H_2S and SO_2 are recoverable products.

In recent decades, many researchers found that manganese-based sorbents exhibited excellent stabilities and high sulfur capacities at high temperatures, though manganese of higher oxidation states is likely reduced to MnO , it does not readily decompose into elemental Mn in a reducing atmosphere [61–63]. Atakül and coauthors [64] performed the sulfidation and regeneration of manganese-based sorbents at the same temperature of 600°C , gas flow rate and H_2S concentration can affect the breakthrough and total capacities, steam was more efficient than hydrogen for regeneration process, and the sulfur-removal rate was proportional to steam content. Bakker and co-workers [65] developed a monolith- or particle-shaped and regenerable manganese-based sorbent for a dry coal gas desulfurization, it consisted of crystalline MnAl_2O_4 , a small amount of dispersing MnO , and an amorphous Mn–Al–O phase; the sulfur uptake capacity was as high as up to 20 g S/100 g at temperature between 1100 and 1200 K, elemental sulfur was the only detected product during regeneration with SO_2 , and the sorbent performance remained stable during at least 110 sulfidation/regeneration cycles at 1123 K.

Wang and co-workers [66] prepared a series of manganese-based sorbents by co-precipitation method for 850°C regenerative H_2S removal, the sulfur capacity increased linearly with the elevation of Mn content, the recovery of elemental sulfur decreased with increase in Mn content as well as O_2 concentration or flow rate of regeneration gas, elemental sulfur was the only product of SO_2 regeneration process; however, the spent sorbents cannot be completely regenerated with SO_2 but it can be completely regenerated by steam, the main product for steam regeneration was hydrogen sulfide. However, the potential disadvantage is that manganese-based sorbents are prone to sulfate formation and must be regenerated at high temperatures. To further improve the performance of the manganese oxides, zinc or copper oxides are doped into them with various Mn/Zn, Mn/Cu molar ratios. Alonso and Palacios [67–69] reported that Zn- or Cu-doped manganese oxides by mechanically mixing the pure MnO_2 and CuO powders in different molar ratios and then calcinating at 950°C exhibited good performances, the structure and degree of

dispersion of the active phases in the fresh and regenerated sorbents as well as those of the sulfides in the spent sorbents were highly dependent on the chemical nature of the dopants, zinc enhanced the formation of mixed oxides or sulfide species, while copper mostly increased the degree of dispersion, these structural and textural changes were consistent with the high sulfidation reactivity of the Mn–Zn and Mn–Cu mixed oxides.

(2) Rare-Earth Oxides

Recently, rare-earth oxides have become a new hot topic in the field of high-temperature desulfurization due to their higher activity and better thermal stability in sulfidation under a strong reductive feed gas as well as the production of elemental sulfur during sorbent regeneration process. Cerium oxide, one of the mostly used rare-earth oxide desulfurizers, can work at a much higher temperature than that of zinc-based desulfurizers, which overcomes the drawback of zinc oxide only working at low temperatures and strong reducing atmospheres, in addition, no cerium sulfates are produced during sulfidation process and the thermal effect is very low. Thus, cerium oxide is regarded as a promising sorbent for desulfurization at high temperatures which is the so-called second generation high-temperature desulfurizers [70]. The hydrogen sulfide concentration was reduced from 1.2% to 3 ppm by using reduced cerium oxide at 872 °C [71]. In 1999, Zeng and coauthors [72] reported that the sulfidation product Ce₂O₂S can quickly react with SO₂ at 500–700 °C temperature range, which directly leads to the generation of elemental sulfur with a molar fraction as high as 20%, and the exothermic amount is very small which is beneficial to prevent the sorbent from sintering, the sulfidation activity of cerium oxide did not only decrease but also showed a good attrition resistance ability after 10 sulfidation-regeneration cycles. And then in 2000, they [73] further studied the influences of temperatures, pressure, air speed, and gas content on the sulfidation ability of the reduced cerium oxide, CeO₂ would be reduced to CeO_{*n*} (*n* < 2) whose sulfidation activity is better than that of CeO₂, the hydrogen sulfide concentration at 850 and 700 °C can be reduced to 10 and 1 ppm, respectively, CeO_{*n*} (*n* < 2) was effectively transferred to Ce₂O₂S after sulfidation, the performance of CeO₂ with pre-reducing treatment is better than that of CeO₂ under simultaneous reduction and sulfidation. Gao and co-workers [74–76] prepared a CeO₂–Fe₂O₃ desulfurizer by mechanically mixing cerium nitrate and red mud with bentonites as additives, the reduction and sulfidation experiments were performed in a fixed-bed reactor under a simulated Texaco coal gas atmosphere at temperatures of 500–800 °C. The surface area of cerium oxide would increase with the elevation of the calcination temperature. The introduction of red mud additive can considerably improve the desulfurization performance of the cerium oxide. The sulfur-removal efficiency increased with the decreasing airspeed; however, the presence of water in the coal gas would inhibit the reduction and sulfidation process, the pre-reduction of CeO₂ can significantly enhance the desulfurization efficiency, the higher of the pre-reduction temperature and the longer of the pre-reduction time, the higher of the sulfur-removal efficiency was.

Though it is difficult to meet the requirement of IGCC coal gas cleaning (H_2S concentration ≤ 20 ppm) by using cerium oxide as desulfurizers, the reduced CeO_n ($n < 2$) has a higher activity than CeO_2 , and it is possible to improve the redox property and sulfidation equilibrium constant of CeO_2 via doping metal oxides for the sake of enhancing its ability for hydrogen sulfide removal [77]. Li and coauthors [78] found that the hydrogen sulfide concentration decreased to as low as 5–10 ppm over CeO_2 – CuO composites in the temperature range of 650–850 °C, the presence of Ce species made the highly dispersed CuO be reduced to metallic Cu, CuO – CeO_2 system transformed into Cu – CeO_x structure, the existence of the reductive cerium oxide is the main reason for the high desulfurization efficiency of CeO_2 – CuO composites [79]. Kobayashi and coauthors [80] prepared series of Cu-doped CeO_2 desulfurizers by using urea co-precipitation sol-gel method. The CuO dispersing in Ce species was reduced to metallic Cu at temperature lower than 453 K. The redox ability of CeO_2 was enhanced due to the presence of Cu species, the surface CeO_2 of 5% Cu-doped cerium oxide can be reduced at low temperature of 423 K. The sulfidation tests in H_2S – H_2 – N_2 feed gas showed that the reductive CeO_2 had a remarkable sulfidation activity even at low temperature of 623 K. Cu-doped CeO_2 can be served as desulfurizers at a broad temperature range of 623–923 K, which makes cerium oxides be extensively used for industrial application. Wang and coauthors [81] also synthesized series of CeO_2 desulfurizers modified with Cu and La atoms by using urea co-precipitation sol-gel approach, and investigated the activity and stability of the Cu, La-modified CeO_2 using for the desulfurization of high-temperature reforming gas. La-modified CeO_2 can effectively alleviate the sintering phenomena of sorbent surface; however, sintering phenomena were observed during the sulfidation of Cu-modified CeO_2 even when the Cu content was as low as 10%, possessed the optimal sulfidation dynamics. Series of CeO_2 – ZrO_2 composites with various Ce/Zr molar ratio were prepared by Yi and co-workers [82], addition of ZrO_2 can increase the surface area of CeO_2 and improve its redox behavior and activity, the hydrogen sulfide concentration in the simulated coal gas can be reduced to as low as 0.1–0.2 ppm in 600–750 °C temperature range, and the breakthrough time of 20% Zr-doped CeO_2 was nearly twofold of undoped CeO_2 .

Flytzani-Stephanopoulos and coauthors [83] adopted CeO_2 – La_2O_3 composites for hydrogen sulfide removal from the solid oxide fuel cell, and they proposed that sulfidation/regeneration conducting at high airspeed can make the reaction occur on the sorbent surface, which resulting in the stable performance of the sorbent, the adsorption of hydrogen sulfide on the fresh or spent CeO_2 and La_2O_3 is reversible, the adsorption and desorption processes are very fast, and any kinds of non-sulfur containing gas mixtures are capable of sorbent regeneration. Yasyerli and co-workers [84] developed CeO_2 – Mn_2O_3 desulfurizers with various Ce/Mn molar ratios, and they were employed for hydrogen sulfide removal at 500 °C. The regeneration performance of the sorbent at 500 and 700 °C was also investigated, doing Mn can significantly increase the sulfur capacity and hydrogen sulfide adsorption rate of cerium oxides, the sorbent with Ce/Mn molar ratio of 3:1 showed the optimal desulfurization performance and good regenerability, the sorbent still

exhibited good sulfidation activity after 10 sulfidation/regeneration cycles, and 90% sulfur species were transformed into elemental sulfur not sulfur dioxide during the regeneration stage. In 2008, Zhao and coauthors [85] studied the COS removal behavior of the Ce-doped Fe₂O₃–Mn₂O₃ composites which showed bigger surface areas and particle dispersion degrees than that of undoped ones, adding Ce can improve their redox properties leading to the enhancement of the Fe₂O₃–Mn₂O₃ composites in sulfur-removal activity, the hydrogen sulfide concentration can be reduced from 15,000 to 0.1 ppm by Ce-modified Fe₂O₃–Mn₂O₃ composites at temperature of 325 °C and airspeed of 1000 h⁻¹; subsequently, they [86] further investigated the effects of Ce, La, Sm addition on the COS removal performances of Fe₂O₃–Mn₂O₃ composites, adding rare-earth elements could increase the sorbent surface areas and enhance the redox abilities in 350–450 °C temperature range, doping 3% La₂O₃ can greatly enhance the adsorption sulfur capacities of the Fe₂O₃–Mn₂O₃ composites under condition of 350 °C and 1000 h⁻¹ as well as reach enough high desulfurization precision before the breakthrough onset. Guo [87] conducted systematic studies on the desulfurization performances of CeO₂-based sorbents; he reported that the microstructures of cerium oxides obtained from various cerium precursors differed from each other, and their reduction and sulfidation abilities were also quite different, the cerium oxide obtained from cerium nitrate showed the optimal reduction and sulfidation activities. The hydrogen sulfide conversions of the CeO₂–CuO composites and CeO₂–Fe₂O₃ composites were both higher than that of pure CeO₂, and both increased with the increasing CuO, Fe₂O₃ amounts as well as the elevation of temperatures. The reduction and sulfidation behaviors of CeO₂–CuO composites can be expressed by improved shrinking core model, and their dynamic parameters at different reaction stages were also obtained. Zhang [88] developed CeO₂–Fe₂O₃ composites obtained by calcination of the iron nitrate-red mud mixtures for high-temperature desulfurization. The sulfidation activities of the desulfurizers with small particle sizes were remarkably better than that of the desulfurizers with big particle sizes. The existence of CO and CO₂ in the feed gas would greatly reduce the sulfidation activity, the optimal reaction temperature of CeO₂–Fe₂O₃ composites was 500 °C, increments in airspeed and inlet hydrogen sulfide concentration would both shorten the breakthrough time and reduce the sulfur-removal efficiency, adding red mud can significantly improve the sulfidation performance. The sorbent remains active after 8 sulfidation-regeneration cycles, and elemental sulfur was detected at the reactor outlet.

The School of chemical engineering of Louisiana State University and Pennsylvania State University had conducted many research works on the desulfurization and regeneration of rare-earth oxides, Dooley and coauthors [89] found that mixed rare-earth oxides (REO) showed a better sulfidation activity at 900 K than that of simply mixed CeO₂ and La₂O₃, Al₂O₃ or ZrO₂ using as the support for rare-earth oxide can increase the sulfur adsorption capacity of the sorbent after many sulfidation/regeneration cycles, its sulfur adsorption capacity can be further increased by doping transition metals (Mn or Fe); however, adding Cu had a little influence on the sulfur adsorption capacity, the undoped REO and transition metal-doped REO both can be regenerated by air and used for sulfidation at least

five times. Though cerium oxide possessed a good stability at high temperature and low hydrogen sulfide equilibrium concentration, it suffers from lower sulfur adsorption capacity compared to transition metal oxides; on the contrary, transition metal oxides, such as CuO and Mn_2O_3 , had higher sulfur capacities and fast sulfidation rates. Thus, Li and coauthors [90] developed CuO– Mn_2O_3 desulfurizers for the sake of combining the good thermal stability and low hydrogen sulfide equilibrium concentration of cerium oxide with the high sulfur capacity as well as the rapid sulfidation kinetics of manganese oxide for hydrogen sulfide capture, and studied the effects of Ce/Mn molar ratios on their desulfurization performances at 900–1023 K, they found that there was a strong cooperative effect between CeO_2 and Mn_2O_3 , the sulfur adsorption capacity would reach a stable value at around 900 K; however, the experimental sulfur capacity was far less than that of the theoretical values based on thermodynamic calculations.

2.4.2 Supported Desulfurizers

The unsupported rare-earth-based desulfurizers showed good thermal stability and high sulfur capacity; however, they often suffer from several problems such as sintering, evaporation, low duration, and bad mechanical strength, which is unfavorable for their industrial applications. Micropore or mesopore materials with high surface areas, big pore volumes, as well as good thermal stabilities using as the supports for the sorbents is a good way to overcome these problems. $\lambda\text{-Al}_2\text{O}_3$ is one of the most extensively used supports for catalysts and sorbents due to its inert property and good thermal stability; Yoo and coauthors [91] studied the sulfidation behavior of $\lambda\text{-Al}_2\text{O}_3$ -supported CuO desulfurizers, they reported that there were three different types (surface, slightly deep, and bulk sulfations) of sulfation reactions of alumina in CuO sorbent, which is determined as a function of CuO loading values and reaction temperatures, surface reaction occurs at CuO loading values 2–11 wt% in 250–350 °C temperature range, slightly deep sulfation happens at CuO content lower than 4 wt% in 350–600 °C temperature range, and bulk sulfation at CuO amount above 6 wt% in 450–600 °C temperature range, and the decrease in sorbent surface area during bulk sulfation was larger than that of at surface sulfation. Yu and co-workers [92] prepared series of $\lambda\text{-Al}_2\text{O}_3$ -supported CeO_2 sorbents with various CeO_2 loading values by using wet impregnation method and studied its sulfidation behavior, regenerability as well as intrinsic kinetics via thermogravimetric technique, monolayer coverage amount of CeO_2 supported on $\gamma\text{-Al}_2\text{O}_3$ was 0.125 g CeO_2 /g $\gamma\text{-Al}_2\text{O}_3$, CeO_2 was uniformly dispersed on $\gamma\text{-Al}_2\text{O}_3$ when CeO_2 was below monolayer coverage, the optimal CeO_2 content was 0.03 g CeO_2 /g $\gamma\text{-Al}_2\text{O}_3$. Ikenaga and coauthors [93] employed carbon materials as the support of ZnFe_2O_4 , such as activated carbon (AC), activated carbon fiber (ACF), and Yallourn coal (YC), the carbon material-supported ZnFe_2O_4 sorbents had larger adsorption capacity for hydrogen sulfide than that of unsupported ferrites, the hydrogen sulfide in a simulated coal gas can be effectively removed from 4000 ppm

to less than 1 ppm at 500 °C, the sulfur absorption capacity of ZnFe₂O₄/AC, ZnFe₂O₄/ACF, and ZnFe₂O₄/YC performed nearly 100% utilization of loaded metal species, they could also be regenerated by a 50 vol.% O₂/Ar gas mixture at 450 °C for 30 min, and the regenerated ferrite can be applied for repeated absorption of hydrogen sulfide with only a very slight decrease in sulfur absorption capacity. Fine coal ash [94] was acted as the support of iron-based sorbents for H₂S and COS removal from hot coal gas at temperatures of 400–650 °C, the experimental results demonstrated that both H₂S and COS can be effectively reduced by using the fine coal ash-supported iron-based sorbents, the enhanced sulfur capacity was achieved owing to the formation of Fe_{1-x}S phase during sulfidation process, COS concentration in hot coal gas stream was strongly associated with the H₂S concentration and played a key role in the removal of COS at high temperatures. Mesoporous SBA-15 [95] and SiO₂ [96] were both used as the support of CuO for hydrogen sulfide removal at high temperatures, SBA-15-supported CuO were prepared by using wet impregnation method, the average breakthrough sulfur uptake capacities after three cycles of 21.97% CuO/SBA-15 and 40.22% CuO/SBA-15 were 0.63 S/100 g and 1.57 g S/100 g, respectively, the sorbent structures were destructed to some extent during the sulfidation-regeneration cycles, and however, their sulfur uptake capacities did not change very much; the sulfidation of amorphous SiO₂-supported nanosize CuO were performed at a laboratory scale fixed-bed reactor through sulfidation-regeneration cycles in the temperature range of 788–838 K at atmospheric pressure, the average sulfur uptake capacities after three cycles at hydrogen sulfide breakthrough point of 20 ppm were in the range of 2.38–2.91 g S/100 g, the high-temperature desulfurization appeared to disturb the structures of the sorbents to some extent, and however, the drop in their sulfur adsorption capacities remained limited.

In recent two decades, Liu's research group at Tianjing University had contributed a lot to the development of mesoporous silica-supported rare-earth oxide desulfurizers prepared by a sol-gel method for hot coal gas desulfurization at high temperatures. In 2011 and 2012, they used MCM-41 and SBA-15 as supports of LaMeO_x (Me = Zn, Co, and Fe) desulfurizers, and the sulfidation tests were performed in a fixed-bed reactor by using a feed gas of H₂S, H₂, CO or CO₂, and balanced with N₂ in 450–700 °C temperature range. The results revealed that 50 wt % La₁Fe₃O₇/MCM-41 (La:Fe = 1:2) sorbent presented the optimal desulfurization performance at 550 °C with a breakthrough sulfur capacity of approximately 5.58 g S/100 g, and appropriate La/Fe ratio in sorbents was a key factor for preparation of high-performance sorbents [97]. The SBA-15 structure of spent LaMeO_x/SBA-15 remained intact after eight successive sulfidation-regeneration cycles, metal oxides supporting on SBA-15 can effectively restrain the mechanical disintegration and improve stability of LaMeO_x/SBA-15; LaFeO₃/SBA-15 with breakthrough sulfur capacity of 4.8 g S/100 g at 500 °C performed better than La₂ZnO₄/SBA-15 and La₂CoO₄/SBA-15, only partial Fe³⁺ ions in LaFeO₃/SBA-15 were reduced by hydrogen in hot coal gas, which is favorable for the sulfidation of LaFeO₃/SBA-15 [98]. LaFeO₃/MCM-41 with breakthrough sulfur capacity of 3.24 g S/100 g at 500 °C exhibited a better sulfidation performance in comparison with La₂ZnO₄/

MCM-41 and $\text{La}_2\text{CoO}_4/\text{MCM-41}$, and its breakthrough sulfur capacity was significantly higher than that of unsupported LaFeO_3 (0.35 g S/100 g, the ten successive sulfidation-regeneration cycle tests revealed that $\text{LaFeO}_3/\text{M41}$ sorbent was stable enough for desulfurization of hot coal gas in chemical industry [99]. Though mesoporous silica (SBA-15 and MCM-41)-supported LaMeO_x desulfurizers showed good thermal stability and durability during several successive sulfidation-regeneration cycles, they suffer from lower sulfur capacities. Since 2012, Liu's research group started to focus on the development of manganese-based desulfurizers. Mn_2O_3 was supported in various mesoporous silica (MCM-41, HMS, and KIT-1) to syntheses 50 wt% Mn_2O_3 /mesoporous silica desulfurizers, the impact of textural properties of mesoporous silica, especially the type of pore channel on the desulfurization performance of manganese-based sorbents was investigated at 600–850 °C, they found that the manganese oxide was highly dispersed in regular pore channels of the mesoporous silica; KIT-supported Mn_2O_3 sorbent showed better desulfurization performance than MCM-41 and HMS-supported Mn_2O_3 sorbents due to its 3D wormhole-like channel, the high sulfur capacity of KIT-supported Mn_2O_3 sorbent (16 g S/100 g) at 800 °C maintained during eight consecutive desulfurization–regeneration cycles, and it still exhibited high desulfurization activity when hot coal gas contained low steam (<5 vol.%) [100]. To enhance the desulfurization efficiency of 50 wt% $\text{Mn}_x\text{O}_y/\text{MCM-48}$ sorbent, the impacts of sorbent synthesis methods (excessive impregnation, precipitation, and sol-gel), precursors ($\text{Mn}(\text{Ac})_2$ and $\text{Mn}(\text{NO}_3)_2$), heating rate during calcination and calcination temperature was systematically investigated, the results revealed that synthesis methods and precursors significantly affected the dispersion of active components while the stable structure of MCM-48 and the dispersion of active particles correlated closely with heating rates and calcination temperatures, which further influences the desulfurization efficiency; therefore, better dispersion of active particles and integrity of MCM-48 structure leads to better desulfurization performance, the best condition was the calcination temperature of 550 °C with a heating rate of 2 °C/min using $\text{Mn}(\text{Ac})_2$ as the precursor by a sol-gel method [101].

To further improve the desulfurization of the mesoporous silica-supported manganese-based desulfurizers, rare-earth metals (Ce, La, and Sm) and transition metals (Zn, Fe, and Mo) were incorporated into the Mn_2O_3 lattice. Cu-doped $\text{Mn}_2\text{O}_3/\text{SBA-15}$ sorbents were synthesized by wet impregnation approach and were used for hot coal gas desulfurization in 700–850 °C temperature range; 1Cu9Mn/SBA-15 after nine successive nine desulfurization–regeneration cycles at 800 °C possessed a high breakthrough capacity of 13.8 g S/100 g owing to the high dispersion of Mn_2O_3 particles incorporated with a certain amount of CuO, which is remarkably higher than those of 40 wt% $\text{LaFeO}_3/\text{SBA-15}$ (4.8 g S/100 g) and 50 wt% $\text{LaFe}_2\text{O}_x/\text{MCM-41}$ (5.58 g S/100 g) at 500–550 °C, which indicating that loading of Mn_2O_3 active species with onto SBA-15 support can significantly increase the sulfur capacity at relatively higher sulfidation temperature, and the SBA-15 structure also remained intact before and after hot coal gas desulfurization [102]. Ce-doped Mn_2O_3 /hexagonal mesoporous silica (HMS) sorbents with

wormhole-like structure were prepared by a sol-gel method and employed for hot coal gas desulfurization at 600 °C, all $x\text{Mn}_y\text{Ce}$ /HMS sorbents presented high breakthrough sulfur capacity, and the utilization of these sorbents was much higher than that of undoped Mn_2O_3 /HMS, 4Mn1Ce/HMS had the highest breakthrough sulfur capacity of 12.17 g S/100 g with utilization of 82.4%, such sulfidation behavior maintained during eight consecutive desulfurization–regeneration cycles [103]. Highly ordered nanorod arrays Mn–Ce metal oxides (MOs) were obtained via negative replication of SBA-15 hard template and were directly employed for hot coal gas desulfurization at 600 °C, 9Mn1CeMOs presented a superior desulfurization activity and small resistance of hydrogen sulfide diffusion as compared to 9Mn1Ce mixed oxides, breakthrough sulfur capacity of 9Mn1CeMOs (19.03 g S/100 g) was much higher than that of $\text{La}_x\text{Fe}_y\text{O}_z$ /MCM-41 (7.94 g S/100 g), it exhibited highly durable regeneration ability during five successive sulfidation/regeneration cycles, parallel nanorod arrays formed with a diameter of 6–7 nm and the nano bridges between the nanorods played a crucial role in the stability of 9Mn1CeMOs [104]. Mn_2O_3 /KIT-6 sorbents were modified by addition of La atoms and applied for hot coal gas desulfurization at temperatures of 700–850 °C, 3La97Mn/KIT-6 performed the best at 800 °C with a breakthrough sulfur capacity of 11.56 g S/100 g as well as endurable regeneration abilities retaining 80% of the initial sulfur capacity after eight continuous desulphurization (800 °C)-regeneration (600 °C) cycles, which indicated a better desulphurization performance as compared to unsupported 3La97Mn and 3La97Mn/MCM-41, the utilization of KIT-6 with 3D pore channels effectively suppressed the aggregation of Mn_2O_3 particles and improved the stability of the sorbent [105]. Mn_2O_3 /KIT-1 sorbents were modified with Mo atoms, the mixed metal oxides were highly dispersed in the wormlike-hole channels of KIT-1 support, and addition of small amount of Mo in Mn/KIT-1 sorbents can significantly improve the sulfur capacity (16.84 g S/100 g) attributed to the synergetic effects of Mn_2O_3 - MoO_3 [106]. Mn_2O_3 /MCM-48 sorbents were modified with Fe and Zn atoms and used for hot coal gas desulfurization, high breakthrough sulfur capacity of 13.2 g S/100 g and utilization of 66.1% over 50% 1Zn2Fe2Mn/MCM-48 at 550 °C were achieved, MCM-48 can remain excellent thermal stability at temperature less than 700 °C, ZnMn_2O_4 and (Mn, Zn) Fe_2O_4 were the mainly active components in fresh sorbents, the decrease in breakthrough sulfur capacity was ascribed to the migration of Zn onto the sorbent surface, and it accumulated on the surface and vaporized to the exterior from the surface [107]. Manganese-based sorbents doped with various rare-earth metals were fabricated via sol-gel method, Mn/MCF exhibited the highest desulfurization performance among Mn/MCM-41, Mn/SBA-15, Mn/MCM-48, and Mn/MCF due to the 3D ultra-large mesopores and excellent thermal stability of MCF at 700 °C, adding rare-earth metals into Mn/MCF promoted the high dispersion of active components, the desulfurization efficiency and precision of Mn/MCF further declined with increasing steam content in feed gas, the induced effects of rare-earth oxides are $\text{CeO}_2 > \text{La}_2\text{O}_3 > \text{Sm}_2\text{O}_3$ [108]. Mo-modified Mn–Fe oxides were supported on a cost-effective mesoporous silica (FSM-16) and were applied for reactive adsorption desulfurization process at temperatures of 550–750 °C,

4Mn1Fe-3%Mo/FSM-16 showed better desulfurization performance at 600 °C with a breakthrough sulfur capacity of 18.15 g S/100 g as compared to unmodified 4Mn1Fe/FSM-16, 90% of its initial sulfur capacity was maintained after multiple sulfidation-regeneration cycles, large amounts of elemental sulfur were produced instead of sulfur dioxide by a simple regeneration, which avoids the further post-treatment of sulfur dioxide, sulfidation-regeneration mechanism was first studied and proposed by highly sensitive TOF-MS technique using $^{18}\text{O}_2$ isotope label [109]. Ca-modified Mn_2O_3 /MSU-H sorbents with excellent steam-resistance ability were synthesized for hot coal gas desulfurization at 600–800 °C, 90Mn10Ca/MSU-H exhibited better sulfidation performance at 750 °C with a breakthrough sulfur capacity of 18.69 g S/100 g compared to other supported Mn-based sorbents, the addition of Ca species acted as a key factor in effectively promoting the dispersion of active constituents, which improved the desulfurization activity; more importantly, the excellent steam-resistance ability of 90Mn10Ca/MSU-H plausibly because that CaO enhanced the sorption of H_2O , and the utilization of MSU-H with large pore size and excellent thermal stability effectively assured fast mass-transfer and confined the migration of active particles, leading to long lifetime stability of sorbents [110].

2.4.3 Kinetic Studies for High-Temperature Desulfurization

High-temperature desulfurization process is a typical gas-solid noncatalytic reaction, its kinetic features are as follows: the reaction not only occurs at the solid surface, but also goes into the inside of the solid pellet, which is a bulk reaction; the particle size and reaction rate changes during the reaction process with time elapsed, which is an unsteady process. The sulfidation process at high temperatures is mainly governed by two stages: one is the chemical reaction control stage, the duration time at this stage is very short due to the fast reaction rate of the high-temperature desulfurization process; another is the diffusion control stage, including the exterior diffusion and interior diffusion of the hydrogen sulfide. The kinetic study which uses a reaction model to describe the influences of different resistances (such as mass transfer, pore diffusion, chemical reaction, and product layer diffusion resistances) on the conversion-time profile poses great importance in developing regenerable oxide sorbents for hot coal gas desulfurization.

In 1982, Ramachandran and Doraiswamy [111] presented a critical review of the developments in the mathematical modeling of the gas-solid noncatalytic reaction with a fairly detailed discussion on the approaches of incorporating structural changes which occur in the solid particles with the progress of reaction, and they pointed out that the structures of the solids played a key role in characterizing the rate of reaction, the porosity, and the pore size distribution of the solid was important parameters for mathematical modeling. In addition, sintering of the solid reactant or product can occur to a considerable extent, in these cases, the effective intraparticle diffusivities are significantly altered by the process of sintering; hence,

it should be determined from independent experiments. During past decades, many kinetic models for noncatalytic gas-solid reactions had been proposed and studied, the shrinking core model (SCM) [112, 113] considers that the reaction occurs at a sharp interface between the reacted outer surface and the unreacted interior core of solid pellets, the gas-solid reaction was regarded as first-order reaction, and the gas diffusion through the solid product layers obeys Fick's law with a constant diffusion coefficient. The unreacted core gradually shrinks while the product layer gradually increases until the whole solid pellet is completely reacted. When the reaction rate is fairly large and the interior gas diffusion resistance is much bigger than that of the chemical reaction (namely the internal gas diffusion process is the rate controlling step), then the shrinking core model is appropriate for describing the sulfidation dynamic process of small particle or micro crystal desulfurizers; however, the gas diffusion rate into solid reactants is orders of magnitude slower than the reaction rate, which is not suitable for solid sorbents of mesoporous structures despite Lee and Koon [114] modified the unreacted shrinking core model by coupling the gas diffusion with the chemical reaction as the rate-limiting step to predict the breakthrough curves of the desulfurization reactions. As we know, solid particles are formed by the accumulation of numerous grains, the pore porosity of solid particles is the gap among the grains, and the dynamics of solid particles is the comprehensive presence of the grain dynamics, the sulfidation reaction resistance coexists with gas diffusion resistance, which plays an important role in sulfidation process. Szekely and Evans [115, 116] proposed the grain model (GM) based on the shrinking core model, the grain model correlates the structure parameters of desulfurizers with their detective micro or macro parameters; however, because the pore porosity lost its subjectivity in the grain model, the diffusion analysis of the pore porosity space becomes more difficult, leading to the complexity in model mathematical solution. Then, they [117] modified the grain model, the grain radius changes during sulfidation reaction as a function of Z which is the ratio between the molar volumes of solid products and solid reactants, the diffusion path, the limit of incomplete solid conversion, can be improved by decreasing the size of the solid pellet. However, this problem can be solved by enhancing the pore volume distribution via a weak acetic acid treatment [118, 119], like metal oxides-supported mesoporous sorbents. GibsonIII and Harrison [120] as well as Ranade and Harrison [121] applied the grain model to express the sulfidation of ZnO, the solid sorbent was presented as an assemblage of non-overlapping grains reacting independently with each other, and each grain was regarded as a shrinking nonporous reactant core, around each grain, reaction with hydrogen sulfide produced a nonporous sulfide product layer.

However, the grain model is inadequately in describing many solid structures, one weakness of the grain model lies in the assumption that the solid is composed of non-overlapping grains where the individual grains grow independently with no overlapping of the product layer. To provide a more realistic description of the solid pellet, Konttinen and co-workers [122, 123] used overlapping grain model (OGM) to study the kinetic behavior of zinc titanate sulfidation or regeneration in a fluidized bed reactor, the activation energies obtained from ambient-pressure TGA

tests for the reaction rate constant and for the product layer diffusion coefficient are 26 and 110 kJ/mol, respectively, which agrees reasonably with previously reported data. For the overlapping grain model, the sulfidation rate is proportional to the reactive internal surface area of the porous pellets, and thus, it follows the real physical behavior of the sorbent in sulfidation more closely than the shrinking core model. However, the grain shapes and porosities of the zinc titanate sorbents should be determined, which practically increases the number of adjustable parameters, thus the shrinking core model with changing effective diffusivity is included due to the possibility of obtaining analytical results without numerical integration, which matches the requirements of a desirable gas-solid reaction model as part of the sulfidation reactor model better than the overlapping grain model. The overlapping grain model was preferred in the modeling of laboratory-scale solid conversion rate data because the parameter values obtained have logical dependence on both process temperature and pressure. For the regeneration of sulfided zinc titanate, its rate was strongly temperature dependent with activation energy of about 140 kJ/mol for the rate constant, the parameters for a uniform conversion model were determined to describe the conversion rate of ZnS regeneration with oxygen [124], then the uniform conversion model was employed for commercial-scale fluidized bed application, the apparent activation energy for the global reaction rate constant obtained from pilot-scale fluidized-bed tests was 200–210 kJ/mol, zinc sulfate formation during regeneration in a pilot-scale fluidized bed was that at sufficiently high temperatures, the partial pressure of oxygen (required for sulfate formation) at the exit of the bed is practically zero so all the possible sulfate formed at lower temperatures will decompose [125]. Lindner and Simonsson [126] represented the initial solid structure as an aggregate of truncated spheres (namely overlapping solid spheres) in contact with each other during the initial stage of sintering, the proposed models differ in their geometric descriptions of the initial structure of the porous solid but they all take into consideration the decreasing diffusion rate in the growing ash layer and the decreasing gas-solid interfacial area at swelling of the solid structure during reaction, because the porous solid undergoes structural changes due to differences in molar volume between solid reactants and solid products in many gas-solid reactions. Sotirchos and Yu [127] further refined this overlapping grain model by representing the solid pellet as an assemblage of grains randomly placed in space with overlapping of the grains, the grain model predicts a monotonically decreasing reaction surface area with conversion and the anomaly of a monotonically increasing pore surface area even when the porosity reduces to zero, but the overlapping grain model is more flexible and powerful than the grain model in that it can predict various behaviors (e.g., a maximum in the rate-conversion profile. Lew and co-workers [128] applied the overlapping grain model which allows for randomly overlapping grains to predict the sulfidation profiles of ZnO and Zn–Ti–O sorbents in 400–700 °C temperature range in which the resistance to reaction is attributed to the diffusion through the product layer and the surface chemical reaction, this model provided a more accurate description of the solids than a non-overlapping model. However, as with all models which try to closely approximate the realistic sulfidation and regeneration behavior, the computational

complexity of the random overlapping grain model is greater than that of the grain model.

Furthermore, Bhatia and Perlmutter [129–131] posed a random pore model (RPM) for liquid-solid reactions, in which a pore structure parameter (ψ) is adopted to express the influence of the structural variation of the solid reactants on the reactivity. The random pore model assumes that pore porosity is a network of random directions and radiuses, a differential equation is introduced to describe the variation of pore porosity, and the tortuosity of pore channels is presented by using a bending coefficient (τ), and however, the measuring of the bending coefficient is very difficult, generally, the bending coefficient is a tunable model parameter. Thus, the random pore model is appropriate for unsupported solids [132, 133]. Then, they correlated the pore structure parameter (ψ) with m serving as the grain shape factor in grain model or the order of reaction in shrinking core model [134]. It is well known that some physical and chemical properties of catalysts would change after chemical reactions leading to variations in the reactivity and selectivity, which is the so-called deactivation of catalysts. The deactivation model (DM) is often applied for catalytic reactions in studying the reasons of the catalyst deactivation as well as the control measures for preventing catalyst from degrading, it can also be employed for the research on the desulfurizer structure variation during the sulfidation process and the influence of the formation of dense sulfide product layer on the desulfurization performance, which can be represented in terms of deactivation rate. Yasyerli and co-workers [135, 136] applied deactivation kinetic model to predict the hydrogen sulfide breakthrough curves of various sorbents, which agrees well with the experimental data. The apparent activation energy and frequency factor as well as the predicted results of the hydrogen sulfide adsorption on a Zn–Mn-based sorbent were studied with the deactivation model, the results of regression fitting revealed the accurate prediction breakthrough behaviors for desulfurization reaction [137]. The deactivation model considering the concentration and temperature dependencies of the desulfurization activity was employed to study the sulfidation behavior of nano-scale high surface area CeO₂, the activation energies were 90 kJ/mol for the deactivation rate constant, which indicates that the hydrogen sulfide adsorption on CeO₂ is chemical adsorption [138]. The kinetic study for the sulfidation of a Zn–Mn-based sorbent (ZMA) was conducted by using the deactivation model, the activation energy of 51 kJ/mol for the deactivation rate constant was relatively lower, indicating that adsorption reaction may occur at a lower temperature, namely ZMA was a good sorbent for hydrogen sulfide from kinetic perspective [139].

Apart from the above models, researchers also developed many other mathematical models for hot coal gas desulfurization over various sorbents. Yoon and co-workers [140] carried out a thermogravimetric investigation of the sulfidation reaction of natural manganese ore, the effects of temperature and concentration of hydrogen sulfide on the reaction rate constant and frequency factor as well as effective diffusivity were studied. The reaction rate constants were obtained from the slope of the initial reaction of TG profiles at negligible external resistance, the order of the reaction was assumed to be first order at 400–600 °C, the activation

energy for the reaction rate constant was 7316 cal/mol. Sun and co-workers [141] derived a ZnO sulfidation kinetic equation integrated into a reactor model of distributed general process modeling system and performed design calculations for desulfurizers in natural gas fuel processing, the effective pore diffusivity of gaseous hydrogen sulfide in the porous zinc oxide pellet was calculated using the general process modeling system, they proposed an ion-migration mechanism which covers a part of the complex chemical process of ZnO sulfidation because the reason that a sulfided or saturated ZnO bed can regain its hydrogen sulfide-capturing capacity after a hot nitrogen treatment, the modeling prediction in simulated desulfurizers was regarded to be subjected to the effect of a long service time, when ZnO/ZnS ion exchange can have a profound impact on altering the saturated adsorption capacity, as well as sulfidation kinetics under a heated environment. Wang and co-workers [142] conducted the study of reaction kinetics and possible mechanism of COS desulfurization over ferric oxide by using thermogravimetric at constant temperature and programmed temperatures, the apparent reaction activation energy was smaller in hydrogen atmosphere than in nitrogen; and the desulfurization reaction of COS takes place more easily in a hydrogen atmosphere. The influence of the reducing temperature played an important part for ferric desulfurization, the optimum temperature for the reducing reaction was under 360 °C, the kinetics of the COS removal reaction are approximately first-order. Hong and co-workers [143] established an improved deactivation kinetic model over mesoporous LaFeO₃/MCM-41 sorbents for hot coal gas desulfurization with mass-transfer correlation based on elementary stoichiometric equation, which consists of both the spatial and the time partial differential equations solved by means of forwarding finite differential method, the kinetic parameters were estimated via nonlinear least-squares fitting, the kinetic model can be used successfully to predict the distributions of hydrogen sulfide concentration at different times and spatial positions within fixed-bed layers, compared to unreacted shrinking core model, random pore model, or grain model. Zeng and co-workers [144] conducted a kinetic study on the sulfidation and regeneration of Mn/Al₂O₃ sorbent for hydrogen sulfide removal at high temperatures. The influence of the reactant gas compositions and temperatures on the sulfidation and regeneration behavior was systematically investigated in a thermogravimetric apparatus. The results showed that the shrinking core model can be used to correlate with the experimental data. The sulfidation was mainly dominated by diffusion, oxygen regeneration had the same situation with sulfidation, and however, for sulfur dioxide regeneration, the regeneration rate was controlled by the chemical reaction in the early stage, and then it is controlled by the diffusion in the latter stage. Long and Loc [145] performed the dynamic studies of the adsorption process modeling by two adsorption models, namely Thomas model and BDST (bed depth service time) model. The kinetic parameters obtained from the models were used to predict the breakthrough time for a larger column which contains the adsorbent about 40 times more than that in the minicolumn experiments, the Thomas model was the suitable model for prediction of 10% initial breakthrough time with an error about 4%.

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