Preparation and SO₂ capture kinetics of a DeSOₓ coating for the desulfurization of exhaust emission

Xing Li a,b,c, Taoli Hu a,d, Tao Zeng b,c, Xiang Ling a, Zhenpeng Wang b,c, Hongyu Huang b,c,* Yong Chen a,b

a School of Mechanical and Power Engineering, Nanjing Tech University, Nanjing 211800, China
b Chinese Academy of Science, Guangzhou Institute of Energy Conversion, Guangzhou 510640, China
c Southern Marine Science and Engineering Guangdong Laboratory (Guangzhou), Guangzhou 511458, China
d Institute of Urban and Rural Mining, Changzhou University, Changzhou 213164, China

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ABSTRACT
Sulfur dioxide (SO₂) is an extremely harmful pollutant in diesel engine exhaust fumes, which must be controlled and removed effectively. In order to better integrate desulfurization materials into diesel exhaust systems, a new desulfurization powder coating (DeSOₓ coating) was prepared. The SO₂ capture performance and kinetics of the DeSOₓ coating were subsequently studied. This study used a fixed-bed reactor to test the DeSOₓ coating SO₂ capture performance and conduct kinetic analysis at various temperatures and gas flows. The analysis obtained the kinetic parameters of the activation energy and Arrhenius constant, with the derived rate control equations, under isothermal conditions. The DeSOₓ coating and filter which were prepared using metal oxide powders, SiO₂ colloidal sol, and additives, exhibited an enhanced SO₂ capture performance. In this experiment, an MnO₂/SiO₂/LiOH coating had the best SO₂ removal rate and capture capacity at 400 °C. Under a reaction space velocity of 10700 h⁻¹, the MnO₂/SiO₂/LiOH coating SO₂ removal rate was 100% within the first hour of reaction. Under a reaction space velocity of 32000 h⁻¹, the MnO₂/SiO₂/LiOH coating SO₂ capture capacity was 132.7 mgSO₂/gmaterial during the second hour of reaction. The SO₂ capture conversion rate of the DeSOₓ coating and filter follows the second-order kinetic mechanism model. For the MnO₂/SiO₂/LiOH coating, the Arrhenius equation gives an activation energy of 4952 J/mol and the Arrhenius natural logarithmic constant is 8.969 s⁻¹. For the MnO₂/SiO₂/LiOH filter, the activation energy of the rate constant is 214 J/mol, and the Arrhenius natural logarithmic constant is 3.744 s⁻¹. Therefore, the desulfurization coating is an effective way to remove SO₂ pollutants from diesel exhaust gases.

1. Introduction

Currently, sulfur dioxide (SO₂) is an extremely harmful component of air pollution. It is mainly produced by fuel combustion, industrial manufacturing, transportation, and a multitude of chemical processes [1]. It is harmful to human health and destroys the ecological environment [2]. SO₂ pollution in the atmosphere causes respiratory, cardiovascular, and nervous system diseases as well as having a toxic effect on a variety of tissues and organs in both humans and animals [3]. SO₂ pollution in the atmosphere can also form acid rain through precipitation, which can lead to the deterioration or even death of plant and animal ecosystems [4]. It can also corrode metal materials, damaging industrial and public facilities, as well as buildings [5]. Therefore, SO₂ in the atmosphere must be effectively controlled and removed. In response, several countries and regions have implemented strict restrictions and regulations on SO₂ emissions.

Diesel engines have several advantages including high power, strong reliability, high thermal efficiency, relatively economical and so on. As a result, they can be widely used in ships, trucks, railways locomotives, agricultural machinery, and other fields [6]. However, despite the advantages, diesel exhaust gases contain numerous harmful components, among which the main pollutants are NOₓ and SOₓ. In addition, due to insufficient diesel engine exhaust regulations, the exhaust gas harmful components usually exceed the standard. Consequently, the harmful exhaust gases require effective treatment during diesel engine usage [7]. If SO₂ in diesel engine exhausts is discharged into the atmosphere, it will
endanger human health and cause environmental pollution. Therefore, whether used in ships or vehicles, SO2 emissions in diesel engine exhaus
ts require strict regulation to prevent the harmful SO2 pollution and also prevent SO2 toxicity with other exhaust catalysts [8].

Diesel engine exhaust desulfurization is more difficult than conven
tional industrial flue gas desulfurization. Diesel engine exhaust desul-
furization requires the setup of a small-space efficient desulfurization system to effectively remove the sulfur dioxide from the exhaust gas [9]. Dry flue gas desulfurization (FGD) technology is a key industrial method for regulating the SO2 pollution emissions in the atmosphere [10]. However, the application of FGD technology in diesel engine exhaust desulfurization is ineffective due to the harsh exhaust conditions. Conven
tional desulfurization materials perform inadequately and cannot effectively remove the SO2 pollutants from diesel engine exhausts. Cur
tent conventional desulfurization materials mainly consist of carbon material, metal oxides, molecular sieve material, organic metal skeleton material, precious metal material, alkali metal material, carbonate material, and other composite materials [11, 12, 13]. However, the desul-
furization performance of different materials varies greatly under different desulfurization conditions. Saha et al. [11] reviewed existing research on a variety of conventional desulfurization materials and found that the desulfurization conditions exert a significant influence on the selection and application of desulfurization materials. Desulfurization conditions below 100 °C usually require materials with strong desulfur-
ization activity and adsorption properties, such as noble metal catalytic materials, carbon materials, molecular sieve materials, organic metal skeleton materials, and other composite materials, which can adsorb and remove SO2 under a low mass transfer driving force. In conditions above 100 °C, the temperature provides more energy to drive the desulfuriza-
tion process. At this time, the desulfurization material needs to possess a certain catalytic activity or react chemically with SO2. Such materials include metal oxides, metal salts, and alkalis, which will catalyze or react with SO2 at a certain temperature, and effectively remove SO2.

The exhaust temperature usually ranges from 150 to 500 °C under diesel engine exhaust desulfurization conditions, therefore, in current conventional desulfurization materials, metal oxides, and their composi
tes, can be used as the main active components, as they are cheap, stable, non-toxic, easily obtainable and possess good desulfurization activity [14]. Mathieu et al. [15] reviewed studies on the removal of SO2 from flue gases by metal oxides and their composites and found that “ideal” desulfurization materials must possess four essential qualities, some of which may appear contradictory to some extent. These are a strong af
finity of the sorbent towards SO2 with fast kinetics, a large specific sur
face area, high physical/thermal/chemical stability, and the capability of multiple regenerations at a practical temperature with performance recov
eries close to 100%. Yu et al. [16] prepared CuO/γ-Al2O3 as a com
posite and recyclable sorbent to remove the SO2 from flue gas, and they found that CuO active component could disperse highly on γ-Al2O3 and the CuO/γ-Al2O3 composite sorbent performs well in the SO2 removal and regeneration. Gaudin et al. [17] prepared CuO/KIT-6, CeO2/KIT-6, and CuO–CeO2/KIT-6 composites for the desulfurization of flue gas, and they found that a compound of CuO and CeO2 on KIT-6 that would have a synergistic effect on the SO2 removal, the CuO–CeO2/KIT-6 composite exhibited the best reactivity among the three synthesized composites. Li et al. [18] prepared several MnOx materials with different physical and chemical structures for the desulfurization of ship exhausts. They found that MnOx desulfurization performance was influenced by pore structure, specific surface area, pore size structure, Mn valence content, and reaction temperature. The pore structure in MnOx considerably affected its desulfurization performance. Zhao et al. [19] prepared micro-sized MgO slurry and MgO nanofluids for the desulfurization of flue gas, and they found that MgO nanofluids had a better desulfurization effect than MgO slurry in the removal of SO2 from flue gas. The desulfurization efficiency increased with increased concentration, while the desulfurization effi
ciency growth rate dropped sharply when the concentration exceeded 4.0 wt%. Mathieu et al. [20] studied the desulfurization process of molecular sieve-loaded metal oxide composites and found that a molecular sieve carrier is mainly used for the dispersion of desulfurization active com-
ponents. The addition of CeO2 oxidizes SO2 to SO3, which combines with active components CuO and Li2O at the active site, to perform chemical adsorption. The reaction then generates CuSO4 and Li2SO4, to realize the adsorption desulfurization process. Yuan et al. [21] studied the influence of physical and chemical properties including crystal structure, element composition, and pore size distribution, on the desulfurization perfor-
manence of multiple metal oxide composites. The physical and chemical structure and characteristics of the composites exhibiting the best desulfurization performance were studied to inform the preparation process and technology of several metal oxide composites. The desul-
furization performance of metal oxides varied greatly under different desulfurization temperatures. According to our previous research [14, 18], manganese oxide (MnO2) had better desulfurization performance than other metal oxides in the desulfurization temperature of 200–500 °C, so MnO2 would be used as the active component to prepare desul-
furization powder coating in our subsequent study.

Functional powder coating is the combination of the powder with various properties including anti-corrosion, antibacterial, high tempera
ture resistance, adsorption, and catalysis, prepared into a powder coating with a specific function [22, 23]. Functional powder coatings vary depending on their field of application. In functional powder coating research and development, we can examine the corresponding functional powder coating, according to the specificity of its intended environment, conditions, and performance. The overall effect of the coating can then be enhanced so that it fully satisfies its function [24, 25]. Consequently, metal oxide desulfurization materials can be prepared into functional powder coating, with specific desulfurization performance, according to the diesel engine exhaust working conditions so that the material func
tions better within the diesel engine exhaust desulfurization system. The application of desulfurization coating in diesel engine exhaust systems is beneficial to both integrate desulfurization material into the tail gas system thus saving space needed for desulfurization, and to optimize, and subsequently improve, the desulfurization coating. Currently, research and application of functional powder coating in diesel engine exhaust purification systems mainly focuses on treating nitrogen oxides and carbon compounds in the exhaust [26, 27]. Most studies use nitrogen oxide or carbon compound catalysts to prepare functional powder coating, before integrating it into the diesel engine exhaust purification system, to achieve the catalytic conversion of nitrogen oxide and carbon compounds in the exhaust gas. However, at present, relatively few studies exist on the preparation of desulfurization materials into func
tional powder coating in diesel engine exhaust purification systems. There is also a lack of experimental and theoretical guidance on desul-
furization functional powder coating. Therefore, studying the prepara
tion of functional powder coating from desulfurization material in diesel engine exhaust purification systems is necessary to open up new and effective diesel engine exhaust desulfurization methods.

In this study, the desulfurization material is prepared as a powder coating, hereafter referred to as DeSOx coating, which can easily be integrated into the diesel exhaust desulfurization system. This saves space needed for desulfurization and utilizes the properties of desul-
furization materials. The DeSOx coating was prepared with metal oxide material as the main active component using a combination of binder and additive. To reveal the intrinsic reaction mechanism between the DeSOx coating and SO2, we provide fundamental information for in
dustrial design, the reaction kinetics of DeSOx coating and SO2 were also studied in this work. The reaction kinetic parameters of DeSOx coating and SO2, including the order of reaction model, rate constant, pre-exponential factor, and activation energy were determined. The kinetic parameters of the desulfurized coating were obtained by studying the DeSOx coating kinetics, so as to guide the desulfurization powder coating preparation.
2. Experiment

2.1. Materials

The manganese oxide particles with a high specific surface area of 253 m²/g (HSSA MnO₂, 99.0%) were supplied by the Japan Metals and Chemicals Co. Ltd., Tokyo, Japan. The manganese oxide nanoparticles (Nano-MnO₂, 50 nm, 99.0%) were supplied by Guangzhou Metal Metallurgy Co. Ltd. The calcium oxide (Nano-CaO, 160 nm, 98.0%), magnesium oxide (Nano-MgO, 50 nm, 99.5%), copper oxide (Nano-CuO, 50 nm, 99.1%), zinc oxide (Nano-ZnO, 50 nm, 99.5%) and iron oxide (Nano-Fe₃O₄, 30 nm, 98.0%) nanoparticles, and anhydrous lithium hydroxide (LiOH, 98.0%), anhydrous lithium chloride (LiCl, 98.0%), and anhydrous sodium hydroxide (NaOH, 96.0%) were purchased from Shanghai Aladdin Bio-Chem Technology Co. Ltd. Silica (SiO₂) colloidal sol was procured from Harbin Jinghuo New Material Co. Ltd. Honeycomb ceramic carrier was bought from Pingxiang Haichuan chemical Co. Ltd. Reaction gas containing 1000 ppm SO₂ + 5% O₂ + N₂ base (99.9%) was bought from Guangzhou Guangqi Gas Co., Ltd.

2.2. Desulfurization coating and filter preparation

Metal oxide powders, SiO₂ colloidal sol, additives, and water are mixed according to a mass ratio of 1:5:0.7:10, before being stirred and ultrasonically shocked to ensure even mixing, to form a coating liquid with a certain fluidity. The carrier to be coated is immersed in the coating liquid until the carrier surface is completely covered with the coating liquid. Excess coating liquid on the carrier surface is blown away following removal from the liquid. The coated carrier is then placed in a dry environment at 200 °C for 2 h, before being allowed to cool naturally to room temperature. After cooling, the coated carrier is re-immersed in the coating liquid, and the entire process is repeated several times. The carrier is then calcined at 400 °C for 2 h. After calcining, it is allowed to cool naturally, and the coating formed on the surface of the carrier is DeSOx coating. The coating on the surface is then collected and ground into powder, which will be used in subsequent performance tests. In addition, in this study, a desulfurization filter element (hereafter referred to as the DeSOx filter) is prepared by coating the DeSOx onto the surface of porous honeycomb ceramic. The honeycomb ceramic carrier is cylindrical, 50 mm in diameter, 20 mm high, with a 2.8 mm diameter square hole. After three impregnations, each honeycomb ceramic carrier is loaded with roughly 4.0–4.5 g DeSOx coating, and the load of each DeSOx filter is about 17.5–19.6 g/ml.

2.3. Desulfurization performance measurement

The crystal structure of the DeSOx coating was analyzed via X-ray diffraction spectroscopy (XRD, X’Pert Pro MPD, Cu Kα radiation), the data was collected in the 2θ range from 5° to 80°, at a scanning velocity of 10°/min. The morphology of the DeSOx coating was observed via scanning electron microscopy (SEM, SU-70, Hitachi Company, Japan). The SO₂ capture performance of the DeSOx coating and DeSOx filter were tested in the fixed-bed reactor [28]. A schematic of the fixed-bed reactor testing system is shown in Figure 1. For DeSOx coating or the DeSOx filter (when testing different samples, the size of the quartz tube used for sample reactions varies), approximately 0.3–1.3 g of DeSOx coating powder or 1–3 DeSOx filters were placed on a quartz tube and then heated to the required temperature. The reactant gas flow, containing SO₂, O₂ and N₂, was regulated by a flow controller. The total gas flow rate was adjustable, and the test reaction gas composition was 1000 ppm SO₂ + 5% O₂ + N₂ base, and the reaction temperature ranged from 100 to 400 °C. The concentration of SO₂ in the reaction gas at the inlet and outlet of the fixed-bed was measured by a flue gas analyzer (Testo 350, Testo SE & Co., KGaA, Germany). The SO₂ concentration at the

Figure 1. Schematic diagram of the fixed-bed desulfurization reactor.
quartz tube outlet decreased over the reaction time ($T$) as $SO_2$ in the reaction gas was absorbed by the DeSOx coating or filter. By measuring the change in $SO_2$ concentration at the quartz tube outlet in real time, the $SO_2$ removal rate, from the reaction gas, by the samples can be expressed by Eq. (1):

$$R_t = \frac{c_i - c_o}{c_o}$$

(1)

where $R_t [%]$ is the $SO_2$ removal rate, $c_i [ppm]$ is the $SO_2$ concentration in the inlet gas, and $c_o [ppm]$ is the $SO_2$ concentration in the outlet gas.

The $SO_2$ capture capacity of the samples can be calculated over a period of time from their $SO_2$ removal rate curves, as shown in Eq. (2):

$$M_t = \int_{t_1}^{t_2} dt \cdot A \cdot m_s \cdot m_c$$

(2)

where $M_t [gSO_2/gmaterial]$ is the $SO_2$ capture capacity accumulated by the samples in time $t [s]$, $m_s [g]$ is the total mass of $SO_2$ accumulated in the quartz within time $t [s]$, and $m_c [g]$ is the mass of the samples.

3. Results and discussion

3.1. The $SO_2$ capture performance of different metal oxide materials

The $SO_2$ capture performance of different metal oxide nanoparticles was measured in a fixed-bed reactor at 150 °C and 350 °C for 1 h, with a reaction gas rate of 100 ml/min (1000 ppm $SO_2 + 5% O_2 + N_2$ base). Figure 2a and b shows the $SO_2$ removal rate curves, and Table 1 presents the $SO_2$ capture capacity and average $SO_2$ removal rate during the first hour of the reaction. According to the results, among several metal oxide materials, only HASS MnO$_2$ and Nano-MnO$_2$ maintained a 100% $SO_2$ removal rate within 1 h, and the HASS MnO$_2$ $SO_2$ capture capacity was higher than that of Nano-MnO$_2$. Therefore, considering the $SO_2$ removal rate and $SO_2$ capture capacity, HASS MnO$_2$ has the best $SO_2$ capture performance of all the metal oxide nanoparticles in our study. This indicates that different metal oxide material activity and $SO_2$ reactions vary significantly at different desulfurization temperatures and that increasing the specific surface area of metal oxide materials is beneficial to $SO_2$ capture. Consequently, in the following research, we use HASS MnO$_2$ as the main active component to prepare the DeSOx coating and filters and add other active components (LiCl, LiOH, NaOH, CuO) to further improve the DeSOx coating performance. In this study, MnO$_2$/SiO$_2$ DeSOx and MnO$_2$/SiO$_2$/LiOH DeSOx coatings were prepared along with MnO$_2$/SiO$_2$/LiOH DeSOx filters.

3.2. The $SO_2$ capture performance of the DeSOx coating

The $SO_2$ capture performance of the MnO$_2$/SiO$_2$ coating doped with different active components was measured in a fixed-bed reactor at 400 °C for 1 h, where the reaction gas (1000 ppm $SO_2 + 5% O_2 + N_2$ base) rate was 200 ml/min Figure 2c shows the $SO_2$ removal rate curves, and Table 1 presents the $SO_2$ capture capacity and average $SO_2$ capture rate during the first hour of the reaction. The results indicate that the addition

![Figure 2](image-url)
of other active components into the MnO2/SiO2 coating can improve the SO2 capture performance. This is because MnO2 plays a major role in desulfurization, and the SiO2 formed by colloidal sol has no desulfurization effect, only a binding effect. Therefore, adding other active components (LiCl, LiOH, NaOH, CuO) to the DeSOx coating can increase the proportion of desulfurization components, thus improving the coating's SO2 capture performance. The reaction quality of the five DeSOx coatings is relatively similar, but only the MnO2/SiO2/LiOH coating can maintain a 100% SO2 removal rate within the first hour following the desulfurization reaction, and it also has a high SO2 capture capacity. This is because among the four adding active components (LiCl, LiOH, NaOH, CuO) in our experiment, LiOH has the highest alkalinity and the best reaction activity with SO2 (an acidic gas) [29]. LiOH can react with more SO2, so the MnO2/SiO2/LiOH coating has the best SO2 capture performance. Therefore, we coated the surface of the porous ceramic carrier with MnO2/SiO2/LiOH to prepare the DeSOx filter.

The XRD patterns of the HSSA MnO2 material, MnO2/SiO2, and MnO2/SiO2/LiOH coating are shown in Figure 3a. The characteristic XRD diffraction peaks of the HSSA MnO2 material exhibit an obvious characteristic peak (PDF#72-1982) and have a good crystal shape. The MnO2/SiO2 coating exhibited an SiO2 characteristic diffraction peak (PDF#46-1045) while retaining the original characteristic HSSA MnO2 (PDF#72-1982) peak. These features indicate that the crystal structure of HSSA MnO2 does not change when in a compound with SiO2 colloidal sol. The characteristic peaks of the MnO2/SiO2/LiOH coating include MnO2 (PDF#72-1982), SiO2 (PDF#46-1045), and LiOH (PDF#32-0564), which indicates that addition of LiOH does not change the crystal structure of the MnO2/SiO2 coating, but instead forms independent components in the DeSOx coating.

SEM micrographs of the HSSA MnO2 material, MnO2/SiO2 coating, and MnO2/SiO2/LiOH coating are shown in Figure 3b-d. The HSSA MnO2 material has a spherical particle structure, with a particle diameter ranging from 0.3-2 um. The MnO2/SiO2 oxide morphology consists of spherical MnO2 particles embedded in an irregular block. The MnO2 active component retains its original spherical shape and silica colloidal sol forms the irregular block material. The MnO2/SiO2/LiOH coating becomes denser and more agglomerated, with irregular small fragments, and more MnO2 particles enclosed within the lumpy solid. In addition, there is no mutual reaction between the MnO2 active component and LiOH, and the function of the silica colloidal sol is to combine different active components to form functional powder coatings. These results are consistent with the XRD results.

Figure 4a and Table 2 show the MnO2/SiO2/LiOH coating SO2 capture performance at different reaction temperatures (100–400 °C). Table 2 shows the reaction gas rate, containing 1000 ppm SO2 + 5% O2 + N2 base, was 200 ml/min. The results show that when the desulfurization temperature ranged between 100 °C and 400 °C, the MnO2/SiO2/LiOH coating penetration time in the fixed-bed reactor increased with desulfurization temperature, and the SO2 removal rate and SO2 capture capacity of the MnO2/SiO2/LiOH coating increased with unit time. These results indicate that desulfurization temperature significantly influences the MnO2/SiO2/LiOH coating SO2 capture performance. As temperature increases, the capture performance also increases, and conversely decreases with decreases in desulfurization temperature. Under the conditions of 30,000 h⁻¹ reaction space velocity, the MnO2/SiO2/LiOH coating SO2 removal rate dropped to zero after 136 min at 100–200 °C but did not drop to zero after 136 min at 300–400 °C. The DeSOx coating capture of SO2 is a chemical adsorption process, through chemical reaction to convert gaseous SO2 to sulfate, so as to remove SO2. Therefore, the increase in desulfurization temperature can provide supplementary energy for the DeSOx coating and SO2 reaction process, which activates more reactive factors needed for the reaction, subsequently promoting the reaction and improving the SO2 capture performance of the DeSOx coating.

Figure 4b displays the MnO2/SiO2/LiOH coating SO2 removal rate curves in a reaction atmosphere of 1000 ppm SO2 + 5% O2 + N2 base, at 300 °C for 2 h, under different gas flow rates. Table 2 shows the corresponding MnO2/SiO2/LiOH coating SO2 capture performance parameters. These results indicate that the reaction gas flow rate also significantly influences the MnO2/SiO2/LiOH coating SO2 capture performance. As the reaction gas flow rate increased, the MnO2/SiO2/LiOH coating penetration time in the fixed-bed reactor decreased, and the MnO2/SiO2/LiOH coating SO2 removal rate and SO2 capture capacity time also decreased. When the reaction quality of the DeSOx coating was constant, its reaction space velocity increased as the reaction gas flow rate increased. The increase of reaction space velocity lead to a reduction in the SO2 residence time in the DeSOx coating, meaning that the DeSOx coating did not have enough time to fully react with SO2, resulting in a decrease in SO2 capture performance.

3.3. The SO2 capture performance of the DeSOx filter

The porous honeycomb ceramic carrier was immersed three times in the MnO2/SiO2/LiOH coating to prepare the MnO2/SiO2/LiOH DeSOx filter, and its sample photos are shown in Figure 5a. As can be seen from Figure 5a, the DeSOx coating can be thickly coated on the porous honeycomb ceramic carrier surface without changing the overall structure of the carrier. In this study, two MnO2/SiO2/LiOH filters were tested in a fixed-bed reactor, where the reaction gas rate, containing 1000 ppm SO2 + 5% O2 + N2 base, was 1100 ml/min, and the MnO2/SiO2/LiOH filter SO2 removal rate curves, at different reaction temperatures (100–400 °C), are shown in Figure 5b. Table 3 shows the corresponding SO2 capture performance parameters of the MnO2/SiO2/LiOH filter. Comparing the MnO2/SiO2/LiOH coating and filter SO2 capture performance at the same desulfurization temperature showed that the SO2 removal rate was higher, and the SO2 capture capacity was lower. This is due to the MnO2/SiO2/LiOH filter’s reaction quality being better, the reaction volume being larger, and the reaction space velocity being smaller. Therefore, the SO2 residence time in the DeSOx filter is higher and the SO2 contact with the DeSOx filter active component is longer, increasing the DeSOx filter reaction efficiency. Therefore, preparation of a DeSOx coating or DeSOx filter is effective ways to the diesel engine exhaust desulfurization systems.
3.4. Analysis of the kinetics of SO$_2$ capture of the DeSO$_x$ coating and filter

In the MnO$_2$/SiO$_2$/LiOH coating, the active MnO$_2$ and LiOH components react with SO$_2$. The reaction between the MnO$_2$/SiO$_2$/LiOH coating and SO$_2$ can be described by two main reaction steps [29], and Eqs. (3) and (4) are as follows:

\[ \text{MnO}_2 + \text{SO}_2 \rightarrow \text{MnSO}_4 \]  
\[ \text{LiOH} + \text{SO}_2 \rightarrow \text{Li}_2\text{SO}_4 \]  

Therefore, the SO$_2$ capture process reaction rate can be parameterized by variables, including temperature, conversion rate, and mechanism. 

Figure 3. XRD patterns (a) and SEM micrographs (b–d) of the HSSA MnO$_2$ material, MnO$_2$/SiO$_2$ coating and MnO$_2$/SiO$_2$/LiOH coating.

Figure 4. The SO$_2$ removal rate curves of the MnO$_2$/SiO$_2$/LiOH coating at different desulfurization temperature (a) and different gas flow rates (b).
The reaction conversion rate during the SO2 capture process can be described by Eq. (5):

\[ \frac{dX}{dt} = k(T)f(X) \]  

(5)

where \( X(t) \) is the conversion rate, \( k(T) \) is the rate constant, and \( f(X) \) is the mechanism function. In most chemical reactions, the relationship between the reaction rate constant \( k(T) \) and reaction temperature \( T \) can be expressed by the Arrhenius Eq. (6).

\[ k(T) = A \exp\left(\frac{E}{RT}\right) \]  

(6)

where \( R \) is the molar gas constant (8.314 J mol/K), \( E \) is the reaction activation energy (J/mol), and \( A \) is the Arrhenius constant.

The SO2 capture conversion rate \( X \) of the MnO2/SiO2/LiOH coating can be calculated using Eq. (7), where \( C_i \) [mol/L] is the cumulative SO2 capture concentration at time \( t \), and \( C_{\text{max}} \) [mol/L] is the theoretical maximum SO2 capture concentration. In the fixed-bed reactor, the SO2 capture conversion rate \( X(t) \) can be calculated from the SO2 removal rate curves.

\[ X(t) = \frac{C_i}{C_{\text{max}}} \]  

(7)

Generally, the reaction mechanism function \( f(X) \) exists in the form of pseudo zeroth, first, and second orders, and so on [32]. For the samples in the fixed-bed reactor, the kinetic reaction model of the pseudo zeroth, first, and second orders are as follows.

The pseudo-zeroth-order kinetic model is shown in Eq. (8):

\[ \frac{C_i}{C_{\text{max}}} = \frac{kt}{C_{\text{max}}} = X \]  

(8)

The pseudo-first-order kinetic model is shown in Eq. (9):

\[ -\ln\left(1 - \frac{C_i}{C_{\text{max}}}\right) = kt = -\ln(1 - X) \]  

(9)

The pseudo-second-order kinetic model is shown in Eq. (10):

\[ \frac{1}{C_i/C_{\text{max}}} = \frac{1}{C_{\text{max}}kt} + \frac{1}{C_{\text{max}}} \]  

(10)

The reaction between the samples and SO2 in the fixed-bed reactor can be split into three stages. In the first stage, SO2 does not penetrate the samples. The continuous reaction between the samples and SO2 makes up the second stage, and the third stage involves the samples reacting with SO2 to reach saturation. In the MnO2/SiO2/LiOH coating and SO2 continuous reaction stage, according to the SO2 removal rate curves at different desulfurization temperatures, graphs of \( X \) and \( t \), \( \ln(1-X) \) against reaction time are plotted.
– \( X \) and \( t \), and \( 1/X \) and \( 1/t \) are drawn, and the reaction order model, with values being the pseudo zeroth, first, and second in the trials, is determined according to the linear relationship of the data in the three graphs.

The relationship diagram between \( X \) and \( t \), \( \ln(1-X) \) and \( t \), \( 1/X \) and \( 1/t \) of the \( \text{MnO}_2/\text{SiO}_2/\text{LiOH} \) coating, at different desulfurization temperatures, are presented in Figures 6a-6c. It can be seen from the linear relationship of the three curves, that the linear relationship between \( 1/X \) and \( 1/t \) is the best match, therefore, the reaction rate constant \( k \) is calculated by the pseudo-second-order reaction model. Linear fitting of \( 1/X \) and \( 1/t \) curves at different reaction temperatures. The reaction rate constant values are obtained from the absolute value of the regression line slope. The reaction rate constant values at different temperatures in our study, with the respective correlation coefficients, are presented in Table 4, where the increase in rate constant values with temperature can clearly be seen.

![Figure 6](image-url)

Figure 6. The relationship diagram between \( X \) and \( t \) (a), \( \ln(1-X) \) and \( t \) (b), \( 1/X \) and \( 1/t \) (c), \( \ln(k) \) and \( 1/T \) (d) at different desulfurization temperatures, and the relationship between \( \ln(\text{dc/dt}) \) and \( \ln c_t \) at different gas flow rates (e) and different \( t \) moment (f).
The logarithm of both sides of the Arrhenius Eq. (6) can be transformed into Eq. (11), in which \( \ln(k) \) and \( 1/T \) conform to a linear relationship. By plotting the corresponding relationship between \( \ln(k) \) and \( 1/T \), the activation energy \( E \) and the Arrhenius constant \( A \) values can be calculated from the slope and linear fitting line intercept in the graph.

\[
\ln(k) = \left( \frac{E}{R} \right) \frac{1}{T} + \ln(A) \tag{11}
\]

Figure 6d is the relationship diagram between \( \ln(k) \) and \( 1/T \), and the activation energy \( E \) and Arrhenius factor \( A \) values are obtained by linear fitting the data in the diagram. As shown in Figure 6d, the linear regression result correlation coefficient is 0.998, the obtained kinetic parameters are \(-595.58\), corresponding to the \(-E/R\) value, and the \( \ln(A) \) value is 2.1938. Consequently, the obtained activation energy \( E \) was 4952 J/mol with an Arrhenius constant \( A \) of 8.969 s\(^{-1}\). The MnO\(_2\)/SiO\(_2\)/LiOH coating reaction rate constant can be expressed as Eq. (12):

\[
k = 8.969e^{-\frac{4952}{RT}} \tag{12}
\]

In addition, the reaction rate between the MnO\(_2\)/SiO\(_2\)/LiOH coating and SO\(_2\) can also be expressed as Eq. (13):

\[
\gamma = \frac{dc}{dt} = kc_t^n \tag{13}
\]

where, \( \gamma \) is the reaction rate (mol/(L\( \cdot \)s)), \( k \) is the reaction rate constant, \( c_t \) is the concentration at time \( t \), and \( n \) is the reaction order.

Eq. (13) is the rate equation of the irreversible reaction, expressed in the form of a power function. Eq. (14) is obtained by taking the logarithm of both sides of Eq. (13).

\[
\ln(\frac{dc}{dt}) = \ln(k) + n\ln(c_t) \tag{14}
\]

As shown in Eq. (14), when the temperature is constant, the reaction rate constant \( k \) is also constant, that is, \( \ln(k) \) is constant, and the plot of

| Isothermal temperature (°C) | Linear regression equation | Correlation coefficient \((R^2)\) | Slope (s) | \( t_{max} \) (s) | \( C_{max} \) (mol L\(^{-1}\)) | Rate constant \((k)\) (L mol\(^{-1}\) s\(^{-1}\)) |
|-----------------------------|-----------------------------|-----------------------------|-----------|-----------------|-----------------|------------------|
| 100                         | \( y = 12281x + 1 \)       | 0.9978                       | 12281     | 5960            | 4.464\(\times\)10\(^{-3}\) | 1.824            |
| 200                         | \( y = 8784x + 1 \)       | 0.9976                       | 8784      | 5960            | 4.464\(\times\)10\(^{-3}\) | 2.550            |
| 300                         | \( y = 7187x + 1 \)       | 0.9999                       | 7187      | 5960            | 4.464\(\times\)10\(^{-3}\) | 3.117            |
| 400                         | \( y = 5969x + 1 \)       | 0.9999                       | 5969      | 5960            | 4.464\(\times\)10\(^{-3}\) | 3.753            |

\(X. Li et al. Heliyon 8 (2022) e11463\)

Figure 7. The relationship diagram between \( X \) and \( t \) (a), \( \ln(1 - X) \) and \( t \) (b), \( 1/X \) and \( 1/t \) (c), \( \ln(k) \) and \( 1/T \) (d) of the MnO\(_2\)/SiO\(_2\)/LiOH filter at different desulfurization temperatures.
In(\(dc/dt\)) against \(In_c\) should be a straight line, with a slope in the reaction order \(n\) of \(c_t\).

According to the MnO\(_2\)/SiO\(_2\)/LiOH coating SO\(_2\) removal rate curves at 300 °C with different reaction gas flows, the relationship between ln(\(dc/dt\)) and ln \(c_t\) at different gas flow rates, is shown in Figure 6e. Figure 6f shows the relationship between ln(\(dc/dt\)) and ln \(c_t\) at different times \(t\). The linear fitting of four points in each group at different moments in Figure 6f, reveal that the linear fitting slope increases as reaction time increases. When the reaction time increased from 580 s to 8580 s, the fitting line slope increased from 1.02 to 1.26. These results show that in the continuous reaction stage (after 520 s) of the MnO\(_2\)/SiO\(_2\)/LiOH coating with SO\(_2\), the reaction mechanism changes from first order to second order with increased reaction time. This is consistent with our second-order reaction model hypothesis.

Moreover, in the MnO\(_2\)/SiO\(_2\)/LiOH filter and SO\(_2\) continuous reaction stage, graphs of \(X\) and \(t\), ln(\(1 − X\)) and \(t\), and \(1/X\) and \(1/t\) are drawn. Figures 7a-7c show the \(X\) and \(t\), ln(\(1 − X\)) and \(t\), and \(1/X\) and \(1/t\) curves of the MnO\(_2\)/SiO\(_2\)/LiOH filter, at different desulfurization temperatures. It can be seen from the linear relationship of these three curves that the linear relationship between \(1/X\) and \(1/t\) is the best match, therefore the reaction rate constant \(k\) is calculated by the pseudo-second-order reaction. The linear fitting of \(1/X\) and \(1/t\) curves at different reaction temperatures. The reaction rate constant values of the MnO\(_2\)/SiO\(_2\)/LiOH filter were obtained from the absolute value of the regression line slope, and the relevant data are presented in Table 5.

Figure 7d is the relationship diagram between ln(\(k\)) and 1/T of the MnO\(_2\)/SiO\(_2\)/LiOH filter. As shown in Figure 7d, the correlation coefficient of the linear regression results is 0.999, and the obtained kinetic parameters of the \(-E/R\) value is -25.685, the ln(\(A\)) value is 1.3202. Thus, the obtained activation energy (\(E\)) was 214 J/mol and the Arrhenius natural logarithmic constant was 8.969 s\(^{-1}\). For the MnO\(_2\)/SiO\(_2\)/LiOH filter, the rate constant activation energy was 214 J/mol, and the Arrhenius natural logarithm was 3.744 s\(^{-1}\). The activation energy of the reaction between the MnO\(_2\)/SiO\(_2\)/LiOH filter and SO\(_2\) was lower than that of the MnO\(_2\)/SiO\(_2\)/LiOH coating, as the MnO\(_2\)/SiO\(_2\)/LiOH coating was suitable for desulfurization of exhaust gas under medium and high temperature, and high reaction space velocity.

Table 5. The rate constant for SO\(_2\) capture as a function of temperature of the MnO\(_2\)/SiO\(_2\)/LiOH filter.

| Isothermal temperature (°C) | Linear regression equation | Correlation coefficient (R\(^2\)) | Slope (s) | \(t_{max}\) (s) | \(C_{max}\) (mol L\(^{-1}\)) | Rate constant (k) (L mol\(^{-1}\) s\(^{-1}\)) |
|-----------------------------|----------------------------|----------------------------------|-----------|---------------|-----------------|-------------------------------|
| 100                         | \(y = 6410x + 1\)          | 0.9999                           | 6410      | 6250          | 4.464\(\times\)10\(^{-3}\) | 3.495                         |
| 200                         | \(y = 6316x + 1\)          | 0.9996                           | 6316      | 6250          | 4.464\(\times\)10\(^{-3}\) | 3.547                         |
| 300                         | \(y = 6255x + 1\)          | 0.9994                           | 6255      | 6250          | 4.464\(\times\)10\(^{-3}\) | 3.581                         |
| 400                         | \(y = 6217x + 1\)          | 0.9993                           | 6217      | 6250          | 4.464\(\times\)10\(^{-3}\) | 3.603                         |

According to the above results, the reaction mechanism models of the MnO\(_2\)/SiO\(_2\)/LiOH coating and the MnO\(_2\)/SiO\(_2\)/LiOH filter with SO\(_2\) agree with the second-order reaction. Since the MnO\(_2\)/SiO\(_2\)/LiOH filter reaction activation energy is lower than that of the MnO\(_2\)/SiO\(_2\)/LiOH coating, it reacts more readily with SO\(_2\). This is because the reacting mass of the MnO\(_2\)/SiO\(_2\)/LiOH filter is large and the reaction space speed is small, therefore contact between the active components and SO\(_2\) is easier, producing the reaction.

4. Conclusions

The DeSO\(_x\) coating is an effective desulfurization approach to diesel engine exhaust system purification, necessitating the accurate estimation of the SO\(_2\) capture performance and kinetics of the desulfurization process. The reaction performance of the DeSO\(_x\) coating with SO\(_2\) was studied in a fixed-bed reactor, the related kinetic parameters were subsequently estimated according to the analysis results of different SO\(_2\) removal rate curves. The results revealed the following:

The DeSO\(_x\) coating and filter, prepared using metal oxide powders, SiO\(_2\) colloidal sol, and additives, demonstrated improved SO\(_2\) capture performance. In our experiment, the MnO\(_2\)/SiO\(_2\)/LiOH coating had the best SO\(_2\) removal rate and SO\(_2\) capture capacity at 400 °C. Under a reaction space velocity of 10700 h\(^{-1}\), the SO\(_2\) removal rate of the MnO\(_2\)/SiO\(_2\)/LiOH coating was 100% within the first hour of reaction. Under a reaction space velocity of 32000 h\(^{-1}\), the SO\(_2\) capture capacity of the MnO\(_2\)/SiO\(_2\)/LiOH coating was 132.7 mgSO\(_2\)/g\(\times\)material within the second hour of reaction. The SO\(_2\) removal rate and SO\(_2\) capture capacity of the DeSO\(_x\) coating and DeSO\(_x\) filter increased as the desulfurization temperature increased and the reaction space velocity decreased. The MnO\(_2\)/SiO\(_2\)/LiOH coating was suitable for desulfurization of exhaust gas under medium and high temperature, and high reaction space velocity.

In the fixed-bed reactor, during the continuous reaction stage between the DeSO\(_x\) coating or DeSO\(_x\) filter, and SO\(_2\), the SO\(_2\) capture conversion rate of the DeSO\(_x\) coating and DeSO\(_x\) filter followed the second-order kinetic mechanism model. For the MnO\(_2\)/SiO\(_2\)/LiOH coating, the Arrenhius equation revealed an activation energy of 4952 J/mol, and the Arrenhius natural logarithmic constant was 8.969 s\(^{-1}\). For the MnO\(_2\)/SiO\(_2\)/LiOH filter, the rate constant activation energy was 214 J/mol, and the Arrenhius natural logarithm was 3.744 s\(^{-1}\). The activation energy of the reaction between the MnO\(_2\)/SiO\(_2\)/LiOH filter and SO\(_2\) was lower than that of the MnO\(_2\)/SiO\(_2\)/LiOH coating, as the MnO\(_2\)/SiO\(_2\)/LiOH filter reaction space velocity is smaller, making contact between the active components and SO\(_2\) easier, therefore producing a easier reaction.

Declarations

Author contribution statement

Xing Li: Conceived and designed the experiments; Performed the experiments; Wrote the paper.

Taoli Huhe; Xiang Ling: Analyzed and interpreted the data.

Tao Zeng: Performed the experiments.

Zhenpeng Wang; Yong Chen: Contributed reagents, materials and analysis tools.

Hongyu Huang: Conceived and designed the experiments; Wrote the paper.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interest's statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.
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