Preparation of a AgCl/PbMoO₄ Composite and Investigation of Its Photocatalytic Oxidative Desulfurization Performance

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ABSTRACT: PbMoO₄ materials were synthesized by the glycerol and hydrothermal methods, and AgCl nanoparticles were loaded onto the surface of PbMoO₄ by using the precipitation−deposition method. Finally, a AgCl/PbMoO₄ photocatalyst was successfully prepared. X-ray diffraction, X-ray photoelectron spectroscopy, scanning electron microscopy, energy-dispersive X-ray spectroscopy, transmission electron microscopy, and UV−vis diffuse reflectance spectroscopy (UV−vis-DRS) were used to characterize the phase composition, morphology, and light absorption characteristics of the catalyst. An n-octane solution of dibenzothiophene (DBT) was used to simulate fluid catalytic cracking to make gasoline. The photocatalytic oxidation performance of DBT under visible light was studied in terms of the type of light source as well as of the catalyst, substrate, and AgCl content. The mechanism of photocatalytic oxidation was also studied. The results show that AgCl loading causes a red shift of the absorption edge of PbMoO₄, which improves the photocatalytic activity of the material. When the AgCl loading was 25.0%, the amount of catalyst was 1.5 g/L, and the visible light irradiation time was 2.0 h, the highest desulfurization rate of DBT reached 97.0%.

1. INTRODUCTION

With the increasing use of automobiles, automobile exhaust has become one of the main sources of air pollution. SOₓ emitted into the atmosphere after the combustion of gasoline not only causes direct harm to the human body but also contributes to acid rain, thereby causing environmental degradation and severely jeopardizing people’s lives. In 2017, China fully implemented the National V Gasoline Standard, which requires the sulfur content to be reduced to 10 μg/g. In China, 90% of sulfur in automotive gasoline comes from fluid catalytic cracking to make gasoline, and the main sulfur compounds are mercaptans, thiophers, disulfides, and thiophenes (Th). Mercaptan sulfur and thioether sulfur are mainly distributed in the light fraction. The C=S bonds of these types of aliphatic sulfides are easy to break, and the lone pair electron density of the S atom is high and can be easily removed by hydridesulfurization (HDS). Th sulfur compounds are mainly distributed in the 60−100 °C fraction and macromolecular Th and benzocyclooctine sulfides are mainly distributed in the heavy fraction. Among these compounds, Th and benzocyclooctine compounds are difficult to remove by traditional HDS technology because of their high steric hindrance and good molecular stability.

Therefore, the key to deep desulfurization of gasoline lies in the removal of Ths and benzothioethers (BTs). At present, nonhydrodesulfurization technologies for desulfurization in-
and visible regions. Molybdate has been widely studied by many researchers. PbMoO₄ has a tetragonal structure of scheelite type, in which each Mo⁶⁺ is surrounded by four “O²⁻ and each Pb²⁺ is surrounded by eight “O²⁻. This complex has a unique crystal structure and a unique energy band structure, with a band gap of approximately 3.20 eV. In recent years, lead molybdate not only has been widely studied in the field of optical instrument manufacturing, photoconductivity, chemiluminescence, and so on but also shows good visible light catalytic activity. In a solution of formic acid and silver nitrate, this complex catalyzes photocatalytic hydrogen production and oxygen production as well as the photocatalytic degradation of organic matter upon ultraviolet irradiation. However, the photocatalytic performance of PbMoO₄ is limited by the visible light absorption and the high recombination rate of photogenerated e⁻ and h⁺, which greatly reduce the catalytic activity of PbMoO₄. Therefore, to solve this problem, AgCl/PbMoO₄ photocatalyst composites were successfully prepared by supporting AgCl nanoparticles on the surface of PbMoO₄, and their photocatalytic performance for the removal of dibenzothiophene (DBT) was studied. During photocatalytic oxidation, the photocatalytic material undergoes an electronic transition after being irradiated with light to generate photogenerated electron–hole pairs. The hole (h⁺) can directly oxidize the organic sulfur model compound adsorbed onto the surface of the photocatalyst and react with H₂O₂ to generate h₂O²⁻, *OH, and O²⁻. These active radicals play an important role in the photocatalytic oxidation system. Therefore, a radical scavenger was added to the photocatalytic oxidation reaction system, and the main active species in AgCl/PbMoO₄ and the mechanism of DBT removal were investigated.

2. EXPERIMENTAL SECTION

2.1. Materials. Pb(NO₃)₂, C₆H₆O₆, (NH₄)₆Mo₇O₂₄·4H₂O, C₆H₁₀OH, AgNO₃, NaCl, BT, DBT, 4,6-dimethyl dibenzothiophene (4,6-DMDBT), Th, n-octane, acetonic acid, sodium hydroxide, sodium molybdate hydrate, cetyltrimethylammonium bromide (CTAB), glacial acetic acid, and deionized water were used. All chemicals used were of analytical reagent grade.

2.2. Characterization. The morphology and the size of the catalyst were characterized using a scanning electron microscope (TESCAN VEGA3) manufactured by Thermo Fisher Scientific (United States). The structure of the catalyst was analyzed using a Rigaku Ultimate IV-type X-ray powder diffraction analyzer produced by Rigaku Corporation (Japan). The experiment used Cu Kα radiation over a scanning range of 10 < 2θ < 80 at a rate of 10°/min, and the tube voltage and current were 40 kV and 40 mA, respectively. The absorption spectrum of the catalyst was obtained using a U-3900H UV–visible diffuse reflection absorption spectrometer produced by Hitachi, Japan, with a wavelength range of 200–800 nm. The elemental composition of the catalyst surface was analyzed using an X-ray photoelectron spectrometer (Thermo ESCALAB250Xi) produced by Thermo Fisher Scientific (United States).

2.3. Catalyst Preparation. 2.3.1. Preparation of PbMoO₄ by the Glycerin Hydrothermal Method. Pb(NO₃)₂ (0.001 mol) was added to 5 mL deionized water and 20 mL glycerin. Then, 5 mL of deionized water containing 0.001 mol of Na₂MoO₄·2H₂O was slowly dropped into the above solution, and the mixture was stirred for 10 min and transferred to a 40 mL stainless steel autoclave. After being treated at 180 °C for 24 h, the solution was naturally cooled to room temperature. The product was washed with deionized water and anhydrous ethanol and then dried under vacuum at 60 °C for 12 h to obtain a PbMoO₄ sample.

2.3.2. Preparation of PbMoO₄ by the Hydrothermal Method. A certain amount of (NH₄)₆Mo₇O₂₄·4H₂O was dissolved in 20 mL deionized water, and 30 mL of 0.5 mol/L CTAB solution was added; the solution was stirred for 30 min and then labeled solution A. A certain amount of Pb(NO₃)₂ was dispersed in 20 mL ultrapure water, mixed with solution A, and stirred for 10 min. After the pH value was adjusted to 5 and 7 with NaOH, the solution was transferred into a Teflon-sealed autoclave for the hydrothermal reaction at 180 °C for 24 h. The obtained dispersion was cooled to room temperature, washed with water and alcohol several times, and dried under vacuum at 60 °C for 12 h to obtain PbMoO₄.

2.3.3. Preparation of AgCl/PbMoO₄ with Different AgCl loadings. First, a certain amount of NaCl solid was dissolved in 25 mL deionized water, and then a certain amount of the prepared PbMoO₄ sample was added. The solution was recorded as solution A, and then, solution A was sonicated for 20 min. The solution was stirred for 1 h, so that Cl⁻ was fully adsorbed onto PbMoO₄ crystals. After that, AgNO₃ (0.1 mol/L) solution with NaCl was added to solution A, and then, the solution was mixed under magnetic force for 6 h in the dark. Finally, the treated solution was centrifuged, washed with water and alcohol several times, and then dried in a vacuum drying oven at 60 °C for 12 h to obtain a white powder sample. To explore the influence of different loading amounts on the catalyst activity, seven control groups were established in this experiment; the total mass of each AgCl/PbMoO₄ sample was 0.3 g, and the samples with different AgCl mass fractions were labeled 0%-AgCl/PbMoO₄, 5%-AgCl/PbMoO₄, 10%-AgCl/PbMoO₄, 15%-AgCl/PbMoO₄, 20%-AgCl/PbMoO₄, 25%-AgCl/PbMoO₄, and 30%-AgCl/PbMoO₄.

2.4. Photocatalytic Oxidation Desulfurization Experiment. A certain amount of DBT was dissolved in 100 mL n-octane solution and mixed thoroughly to prepare a model oil solution with a sulfur content of 200 mg/L. From that solution, 30 mL was removed, which, along with an appropriate amount of catalyst and oxidant, was added to a 50 mL quartz tube. The quartz tube was placed in a photochemical reactor, which was magnetically stirred for 30 min in a dark environment to achieve adsorption–desorption equilibrium. Then, the xenon lamp was turned on, and 5 mL samples were taken every 30 min. Then, the acetonitrile fraction of the above solution was collected. Finally, the upper solution was collected, and the sulfur content was determined with a WK-2D microcoulomb analyzer. By comparing the results with the sulfur content of the original solution, the desulfurization rate was obtained, and the desulfurization effect was analyzed. The desulfurization rate was calculated according to formula 1, where η is the desulfurization rate and C₀ and Cₜ are the sulfur contents of the solution before and after the reaction, respectively.

\[ \eta = \frac{C_0 - C_t}{C_0} \times 100\% \] (1)

3. RESULTS AND DISCUSSION

3.1. X-ray Photoelectron Spectroscopy Analysis of AgCl/PbMoO₄. As shown in Figure 1a–d, the binding
energies of different valence states of various elements in the PbMoO₄ catalyst were studied by X-ray photoelectron spectroscopy (XPS) to analyze the composition and the chemical state of PbMoO₄ microcrystalline particles. Figure 1a shows the general XPS spectrum of the PbMoO₄ photocatalyst, which shows the best catalytic activity compared with other samples. The spectrum clearly shows that the photocatalyst was composed of Pb, Mo, O, and C (elements inherent in the system), and no other impurity peaks were detected. The inner layer electron binding energy of Mo 3d is shown in Figure 1b. The Mo 3d peaks observed at 234.9 and 231.8 eV were ascribed to the chemical valence states of Mo⁶⁺ of MoO₃ and represent Mo 3d⁵/₂ and Mo 3d³/₂, respectively. The 3d bimodal split was approximately 3.0 eV.²⁹ Figure 1c shows the inner layer electron binding energy of Pb 4f. There were two characteristic peaks of Pb 4f at 138.1 and 142.9 eV, corresponding to Pb 4f⁷/₂ and Pb 4f⁵/₂, respectively. These two peaks were mainly attributed to PbO, which originated from the Pb⁺⁺ in PbMoO₄.²⁹ Figure 1d shows a characteristic diagram of the inner electron binding energy of O 1s, which shows three peaks. The peak at 529.2 eV corresponds to the lattice oxygen of the sample. The binding energy at 530.0 eV is attributed to Mo—O, and the peak at 531.5 eV is characteristic of Mo—OH. The above analysis results were consistent with the X-ray diffraction (XRD) results.

As shown in Figure 2a–f, to further analyze the composition and chemical states of the elements in AgCl/PbMoO₄ microcrystalline particles, the binding energies of different valence states of the elements were investigated by XPS. Figure 2a shows the general XPS spectrum of the AgCl/PbMoO₄ photocatalyst, which exhibited better catalytic activity than the other samples. It can be clearly seen from the spectrum that the photocatalyst was composed of Pb, Mo, O, Ag, Cl, and C (elements inherent in the system), and no other impurity peaks were detected. Figure 2b shows two characteristic absorption peaks at 367.9 and 373.9 eV attributed to the inner electron bonding energy of Ag 3d, corresponding to Ag 3d⁵/₂ and Ag 3d³/₂, respectively. The positions of these two characteristic absorption peaks were exactly consistent with Ag⁺, and the characteristic absorption peaks at 368.8 and 374.3 eV can be attributed to Ag⁰. It can be seen that a small amount of Ag metal was formed in AgCl/PbMoO₄, which was consistent with the result of XRD. Moreover, as shown in Figure 2c, the binding energies of 198.1 and 200.1 eV correspond to Cl 2P³/₂ and Cl 2P₁/₂, respectively, thus proving the existence of Cl⁻. Figure 2d shows the inner layer electron binding energy of Mo 3d, and the peaks of Mo 3d were at 234.9 and 231.8 eV, which represent Mo 3d⁵/₂ and Mo 3d³/₂, respectively. These peaks were attributed to the Mo⁶⁺ state of MoO₃, and the split of the 3d double peaks was approximately 3.0 eV. Figure 2e shows a characteristic diagram of the inner
The electron binding energy of O 1s, which shows three peaks. The peak at 529.2 eV corresponds to the lattice oxygen of the sample. The binding energy at 530.0 eV is attributed to Mo−O, and the peak at 531.5 eV is characteristic of Mo−OH.

Figure 2f clearly shows the inner layer electron binding energy of Pb 4f. There were two characteristic peaks of Pb 4f at 138.1 and 142.9 eV, corresponding to Pb 4f 7/2 and Pb 4f 5/2, respectively. These two peaks were mainly attributed to PbO, which originated from the Pb2+ of PbMoO4. The results of the abovementioned analysis were consistent with the XRD results.

From Figure 3a−d, it can be seen that the crystallinity of each sample was excellent. The characteristic diffraction peak 2θ and d values of each sample showed a good agreement with the PbMoO4 standard card (44-1486) of the tetragonal molybdenite-type structure, and there was no impurity peak, indicating that the purity of the obtained material was relatively high. Figure 3e shows the XRD patterns of AgCl/PbMoO4, which contain all the diffraction peaks of the PbMoO4 photocatalyst. As seen in Figure 3e, the AgCl/PbMoO4 composite gives rise to diffraction peaks at 2θ = 27.80, 32.20, 46.23, and 57.44°, which could be assigned to the (111), (200), (220), and (222) crystal planes of AgCl (31-1238), indicating that AgCl and PbMoO4 were present in the AgCl/PbMoO4 sample. The reflection at 2θ = 54.8° could be assigned to the (311) crystal plane of Ag. According to the limited conditions of the control reaction to avoid light, part of the AgCl was decomposed into Ag. There were no other heteropeaks in the XRD, which indicated that the photocatalyst shows high purity. There are no obvious differences in the crystallinity and the phase composition of the catalysts prepared using different conditions and methods after analysis, but considering the principle of using the least number of chemical synthetic steps, the catalysts prepared by the glycerin method are preferred in this paper.

3.2. Scanning Electron Microscopy Analysis of PbMoO4 and AgCl/PbMoO4. Figure 4a−d shows the field
3.3. Energy-Dispersive X-ray Spectroscopy Analysis of PbMoO₄ and AgCl/PbMoO₄. The energy spectrum and the element content distribution curve of the PbMoO₄ catalyst are shown in Figure 5a–e. Polyhedral PbMoO₄ particles contain only Pb, Mo, and O and have obvious distributions with no other impurities. The elemental ratio of Pb, Mo, and O was 1:1:4, confirming that the PbMoO₄ material with high purity was prepared (Figure 5e). Figure 6a–f shows the energy spectrum of the AgCl/PbMoO₄ composites (after photocatalytic performance testing, this catalyst was the best performing group, so according to the principle of optimal performance, a series of characterization analyses were conducted for only AgCl/PbMoO₄). As shown in the energy spectrum, the sample was composed of five elements: Ag, Cl, Pb, Mo, and O. The atomic ratios of these five elements were Ag/Cl = 1:1 and Pb/Mo/O = 1:1:4. This result also proved that the AgCl/PbMoO₄ composite material was composed of AgCl and PbMoO₄.

3.4. Transmission Electron Microscopy Analysis of AgCl/PbMoO₄. To further analyze the structure and morphology of the AgCl/PbMoO₄ composites, this experiment used transmission electron microscopy (TEM) and high-resolution (HR) TEM to analyze the microstructure and the interface composition of these composite materials. Figure 7a–d shows the TEM images of the AgCl/PbMoO₄ photocatalyst. The results show that the morphology of AgCl/PbMoO₄ consisted of uniform octahedral structures, and the results were consistent with the SEM results. It can be seen from the figure that some particles were distributed on the surface of the PbMoO₄ structure, and the TEM results were consistent with the SEM results. More evidence for AgCl on the surface of PbMoO₄ is further provided by HR-TEM (Figure 7f). The HR-TEM images correspond to Figure 7c. The HR-TEM results show clear lattice fringes with d-spacing of 0.16 and 0.28 nm belonging to the lattice fringe of the (222) and (200) planes for AgCl. The d-spacing of 0.32 nm corresponds to the (112) planes of PbMoO₄. The results prove that AgCl was successfully loaded onto the surface of PbMoO₄ as shown in the figure.

3.5. UV–vis Diffuse Reflectance Spectroscopy Analysis of PbMoO₄ and AgCl/PbMoO₄. The light absorption properties of semiconductors affect the photocatalytic activity of the catalyst. Figure 8 shows the UV diffuse absorption spectra of PbMoO₄ and AgCl/PbMoO₄ photocatalysts. As is shown, both materials have strong light absorption between 250 and 380 nm. The absorption edge of each sample is different; the absorption edge of PbMoO₄ is at 392 nm, while that of AgCl/PbMoO₄ is significantly red-shifted to 410 nm, indicating that the AgCl/PbMoO₄ composite has stronger visible light absorption. The analysis shows that the AgCl/PbMoO₄ composites obtained by loading AgCl particles onto PbMoO₄ by precipitation–deposition improved the visible light response to some extent, which was also beneficial for the generation of electron–hole pairs and the photocatalytic activity. The relationship between the band gap and the band edge absorption of a semiconductor material is

$$\lambda_g = \frac{1}{E_g}$$  

where $$\lambda_g$$ is the absorption edge. The band gaps of PbMoO₄ and AgCl/PbMoO₄ were calculated to be 3.16 and 3.02 eV, respectively. The recombination of AgCl and PbMoO₄ reduced the band gap value of the catalyst and improved the visible light absorption capacity of the AgCl/PbMoO₄ composite. In the photocatalytic process, photo-

Figure 3. XRD patterns of PbMoO₄ and AgCl/PbMoO₄. (a): PbMoO₄ samples prepared by the glycerin method; (b): PbMoO₄ at pH = 5 (180 °C CTAB); (c): PbMoO₄ at pH = 7 (180 °C CTAB); (d): PbMoO₄ at pH = 7 (170 °C CTAB); and (e): AgCl/PbMoO₄.

Figure 4. (a,b) SEM images of PbMoO₄ and (c,d) SEM images of AgCl/PbMoO₄.
generated electrons and holes were more easily generated, and the activity of the material was also improved.

4. CONCLUSIONS

In this paper, PbMoO₄ polyhedral crystallites were synthesized by glycerol and hydrothermal methods. The AgCl/PbMoO₄ photocatalyst was successfully prepared by the precipitation–deposition method. The composite materials were characterized by various methods. The analysis results proved that AgCl was successfully supported on the PbMoO₄ surface, and a significant redshift occurred, improving the response to visible light. Using DBT as the removal target, the photocatalytic oxidation desulfurization performance of AgCl/PbMoO₄ under visible light was investigated under different reaction conditions, and the photocatalytic oxidation mechanism was explored. The experimental results show that the desulfurization performance of AgCl/PbMoO₄ for different organic sulfur compounds in gasoline is DBT > 4,6-DMDBT > BT > Th. When the loading of AgCl was 25.0%, the amount of catalyst was 1.5 g/L, and the removal rate of DBT was up to 97.0% after 120 min of light irradiation, indicating that the photocatalytic activity of the composite was much higher.
than that of pure PbMoO$_4$. The AgCl/PbMoO$_4$ composite was used in the recycling experiment. After being reused five times, the removal rate of DBT by the composite catalyst was only reduced to 90.0%, which showed that the AgCl/PbMoO$_4$ composite catalyst has good stability. At the same time, radical capture experiments show that O$_2^-$ and h$^+$ are the main active species in the photocatalytic oxidation process.

4.1. Effect of AgCl/PbMoO$_4$ on Photocatalytic ODS.  
4.1.1. Effect of Light Source Types. The conditions of the photocatalytic reaction exert significant influence on the catalytic activity, and the light source is an important factor. Different light sources have different distributions, so they have different effects on the photocatalytic activity of the catalyst.

Figure 9 shows the experimental results obtained with a high-pressure mercury lamp and a xenon lamp. PbMoO$_4$ has the highest catalytic activity for DBT when a mercury lamp is used. The main reason for this finding is that in the wavelength range of 200–400 nm, the high-pressure mercury lamp has a strong spectral distribution, while the xenon lamp is very weak. The spectral distribution of sunlight in the range of 300–1000 nm is relatively uniform. The UV-DRS spectra show that in the range of 200–400 nm, PbMoO$_4$ has strong absorption. Therefore, in this experiment, a high-pressure mercury lamp was used as the light source for the reaction. The photocatalytic activity was relatively good, and the DBT removal rate achieved was 94.0%.

Figure 6. (a) Gray scale of AgCl/PbMoO$_4$. (b) Cl element distribution of PbMoO$_4$. (c) Mo element distribution of PbMoO$_4$. (d) Ag element distribution of PbMoO$_4$. (e) Pb element distribution of PbMoO$_4$. (f) EDS spectrum of AgCl/PbMoO$_4$. 

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4.1.2. Effect of the Amount of Photocatalyst. To research on the desulfurization ability of AgCl/PbMoO₄, the influence of the amount of catalyst used on DBT removal was explored. The analysis results are shown in Figure 10. First, 0, 6, 12, 18, 24, and 30 mg of the AgCl/PbMoO₄ photocatalyst (concentrations of 0, 0.3, 0.6, 0.9, 1.2, and 1.5 g/L, respectively) were added to 20 mL model oil with a sulfur content of 200 mg/L. At a constant reaction time, the use of more photocatalyst resulted in a higher DBT removal rate. After reacting for 120 min, when the amount of photocatalyst was sequentially increased from 0 to 30 mg, the DBT removal rate gradually increased to 97.0%. When the amount continued to increase, the removal rate did not increase because the reaction reached a saturation state. As the amount increased, the number of active sites available for the reaction gradually
increased, but when the reaction system reached a saturation state, the photocatalyst agglomerated, the number of exposed active sites decreased, and the removal effect was reduced. Therefore, the optimal amount of photocatalyst was determined to be 1.5 g/L.

4.1.3. Effect of the Loading of AgCl. The loading of AgCl was an important factor affecting the efficiency of the photocatalytic oxidation reaction. To study the effect of AgCl loading on the desulfurization rate of DBT, 0%-AgCl/PbMoO₄, 5%-AgCl/PbMoO₄, 10%-AgCl/PbMoO₄, 15%-AgCl/PbMoO₄, 20%-AgCl/PbMoO₄, 25%-AgCl/PbMoO₄, and 30%-AgCl/PbMoO₄ were prepared. Their removal efficiencies for DBT were studied. Figure 11 shows that with the same reaction time, the removal efficiency of DBT increased gradually as the AgCl loading amount increased. When the loading amount of AgCl increased from 0 to 25%, the DBT removal efficacy increased from 56.0 to 97.0% because when the loading amount of AgCl was 25.0%, there were more active sites at a high loading amount of AgCl/PbMoO₄ than at a low loading amount of AgCl/PbMoO₄. However, an excess of AgCl (30%) reduced the removal efficiency. One possibility was that excessive loading led to serious aggregation, resulting in a decrease in the number of active sites of AgCl/PbMoO₄. Another possible reason was that 25% AgCl loading on the surface of PbMoO₄ had the best dispersion, so the desulfurization rate would not change as the AgCl loading amount was increased. Thus, the optimal loading amount of AgCl was determined to be 25.0% with an excellent desulfurization rate of 97.0%.

4.1.4. Degradation Rate of Different Sulfur-Containing Model Compounds. To investigate the degradation rate of AgCl/PbMoO₄ on different substrates (sulfides), BT, Th, and 4,6-DMDBT were used as new model sulfur compounds in the reaction system to prepare a new n-octane solution with a sulfur content of 200 mg/L. Under the same experimental conditions, only the type of sulfur-containing substrate was changed, and the desulfurization rate was compared. As shown in Figure 12, the best desulfurization rate was achieved for DBT, followed by 4,6-DMDBT, then BT, and finally Th. After 120 min of reaction, the desulfurization rate of DBT was 97.0%, while that of Th was only 53.0%. Therefore, the order of removal efficiency of various model compounds was DBT > 4,6-DMDBT > BT > Th. This conclusion may be because of the influence of steric hindrance of the methyl groups and the electron cloud density of the S atom. The electron cloud densities of the S atom in Th and BT were 5.739 and 5.696, respectively, while those of 4,6-DMDBT and DBT were 5.760 and 5.758, respectively. The S atom electron cloud of Th had the lowest density and was the most difficult to oxidize; therefore, its degradation rate was far lower than those of 4,6-DMDBT and DBT. The S electron cloud densities of 4,6-DMDBT and DBT are very similar, indicating that their activities are also similar, so it is difficult to distinguish these complexes. Therefore, the degradation rates of these two sulfides are mainly affected by the steric hindrance of the methyl group, which reduces the chance of contact between active species and S atoms. Because there is a dimethyl group in 4,6-DMDBT, the degradation rate of 4,6-DMDBT is lower than that of DBT.

4.1.5. Cycling and Stability of the Catalyst. To study the cycling performance and the stability of the catalyst, the used photocatalyst was recovered, filtered, and dried for use. Under the conditions of high-pressure mercury lamp irradiation for 2.5 h, a catalyst dosage of 1.5 g/L, and 30 mL model oil with a sulfur content of 500 mg/L, the effects of photocatalyst usage on the desulfurization efficiency of the DBT model oil were investigated. The experimental results are shown in Figure 13.
It can be seen from Figure 13 that after five times of recycling, the desulfurization rate of photocatalytic oxidation was reduced from 97.0 to 90.0%, indicating that the catalyst still has good activity after recycling. When the catalyst was used for the sixth time, after 2.5 h of reaction, the desulfurization rate was only reduced to 90.0%, indicating that the catalyst has good stability.

4.2. Desulfurization Mechanism. 4.2.1. Determination of Active Radicals. To investigate the main active species in the AgCl/PbMoO₄ photocatalytic reaction system, 1 mM concentrations of the radical scavengers isopropanol (IPA), sodium oxalate (Na₂C₂O₄), and p-benzoquinone (1,4-BQ) were used to capture h⁺, -OH, and -O₂⁻, respectively. To remove the interference of DBT itself by the three radical scavengers, a group of control experiments was done. There was no direct relationship between the radical scavenger and the DBT removal efficiency, as shown in Figure 14. As shown in Figure 13a,b, after 2 h of reaction, the desulfurization rates with Na₂C₂O₄ and 1,4-BQ as the radical scavenger decreased from 97.0 to 42.0 and 26.0%, respectively, indicating that the photocatalytic activity was inhibited. This result shows that during the photocatalytic degradation process, h⁺ and -O₂⁻ were generated and participated in the reaction. Figure 14c shows that the DBT desulfurization rate was almost unchanged after adding IPA to the reaction system for 2 h. Therefore, it can be concluded that -O₂⁻ and h⁺ were the main active species in this process.

4.2.2. Study of the Mechanism of Photocatalytic Reaction. It can be seen from the abovementioned radical analysis that the main active species in the AgCl/PbMoO₄ composite photocatalytic oxidation system are holes and superoxide radicals. However, because the activity of the catalyst is closely related to its band gap width, the reaction mechanism was analyzed. The E_g value of PbMoO₄ is 3.16 eV, while the E_g value of AgCl is 3.25 eV.³¹,³² From the empirical formulas 2 and 3, the positions of the conduction band (CB) and the valence band (VB) of AgCl and PbMoO₄ were calculated. The values are listed in Table 1.

\[ E_{VB} = X - E^e + 0.5E_g \]  
\[ E_{CB} = E_{VB} - E_g \]

Based on radical capture experiments and energy band results, a schematic diagram of the photocatalytic oxidation mechanism is shown in Figure 15. Because of the wide band gaps of PbMoO₄ and AgCl, both can be excited by visible light. According to the VB structure characteristics of PbMoO₄ and Ag/AgCl, the composite material can be transformed into Z-type Ag/AgCl/PbMoO₄ under visible light irradiation. The Fermi level of metallic Ag is 0.4 eV, which is higher than the CB potential of PbMoO₄ (−0.1 eV). Therefore, under the action of the interface Schottky barrier, an e⁻ on the CB of PbMoO₄ is very easy to inject into metal Ag. The potential of the AgCl VB (3.19 eV) is higher than the Fermi level of Ag metal (0.4 eV), and thus the e⁻ on Ag metal is transferred to the AgCl VB. Ag particles can transport photogenerated electron–hole pairs, which can transfer electrons from the CB of PbMoO₄ to the VB of AgCl. At the same time, photogenerated electrons can reduce the O₂ adsorbed onto AgCl to give superoxide radicals. Superoxide radicals have

![Figure 13. Recycling performance of AgCl/PbMoO₄.](image1)

![Figure 14. Relationship between the desulfurization rate and time with different radicals: (a) Na₂C₂O₄ (b) 1,4-BQ, and (c) IPA.](image2)

![Figure 15. Schematic diagram of the photocatalytic oxidation mechanism.](image3)

Table 1. Electronegativity, Band Edge, VB Position, and Band Gap Energy of AgCl and PbMoO₄ Semiconductors

| Semiconductor | X/eV | E_{VB}/eV | E_{CB}/eV | E_g/eV | E'/eV |
|---------------|------|-----------|-----------|--------|-------|
| AgCl          | 6.04 | 3.19      | −0.06     | 3.25   | 4.50  |
| PbMoO₄        | 5.98 | 3.06      | −0.1      | 3.16   | 4.50  |
strong oxidizing properties and can oxidize the DBT molecules on the catalyst surface. The h+ remaining on the PbMoO4 surface can oxidize DBT. Because the VB (+3.19 eV) of AgCl is more correct than that of PbMoO4 (+3.06 eV), the h+ on the VB of AgCl can be transferred to the VB of PbMoO4, where OH− can be oxidized to *OH, which has a strong oxidizing effect on DBT. According to the above analysis and the results of the radical capture experiment, after being irradiated by visible light, there were three kinds of active species in the reaction system, namely, h+, *OH, and *O2−, but the main active species were *O2− and h+.

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**Notes**

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