



Preparation and Properties of Supported Mg-Al Hydrotalcite Layered Composite Photocatalyst

Mande Qiu*, Mengli Shang, Yanlong Cui, Xu Bian

College of Chemistry and Environmental Science, Hebei University, Baoding 071002, People's Republic of China

Abstract In this study, a composite photocatalyst material (TiO₂/MgAl-LDH) was synthesized by a simple wet-chemical method together with nano-scale TiO₂ as photocatalyst and Mg-Al layered type hydrotalcite of modified by tetrabutyl titanate sol. Slight crystallization MgAl-LDO is subsequently made from MgAl-LDH by calcination. The characterization by X-ray diffraction, scanning electron microscopy and energy dispersive spectrometer showed phase, surface microstructure and photocatalyst loading state before and after calcination. To evaluate its photocatalytic performance, the MgAl-LDO was used for the degradation of methyl orange contaminant from wastewater prior to UV-Vis spectrophotometer analysis. The result showed that the MgAl-LDO had a higher specific surface area than before burn. Under UV irradiation, the as-prepared TiO₂/MgAl-LDO composite photocatalyst showed the higher photocatalytic degradation efficiency because of its coupling photocatalytic degradation and adsorption decolorization. In this process, adsorption plays a predominant role in the initial stage of decolorization and the TiO₂ plays the leading role after adsorption equilibrium. The methyl orange were degraded with the MgAl-LDO composite, which has 60 mg (TiO₂: MgAl-LDO=1) by weight of catalyst, obtaining up to 90% of degradation during 60 min of reaction.

Keywords TiO₂; MgAl-LDH; composite photocatalyst; microstructure.

1. Introduction

In recent years, the application of semiconductor photocatalytic oxidation technology to the treatment of environmental pollutants has become the hot topic in environmental science research. Among numerous semiconductor photocatalyst, the TiO₂ is considered as the most promising photocatalyst due to its high photocatalytic activity, stability, and no secondary pollution [1-2]. Nevertheless, due to its agglomeration effect, easy to inactivate, difficult in recycling and so on, nano-scale TiO₂ powder is hampered on further application and development [3]. Hence, the research of supported photocatalyst has always been an important content in the field of photocatalytic research.

At present, the research of supported photocatalyst has been focused on carrier selection, immobilization technology and carrier effect mechanism. The appropriate carrier materials does not only improve the effective surface area of the reaction, provide appropriate pore structure, and improve the mechanical strength of the catalyst, thermal stability and anti-toxic properties, but also enhances the photocatalytic reaction without altering the photocatalyst performance [4-5]. In many carriers, the hydrotalcite type compound possess some specific characterized by its characteristics of alkaline, cation-adjustability on the layer and exchangeability of interlayer anions, due to its special anionic layered structure [6] and have been applied in many field. Especially, its combustion products have



been widely used in the treatment of pollutants due to their high absorptivity [7]. However, if adsorbents only have physical adsorption, it is easy to cause secondary pollution. Thus, there is an important practical significance for the utilization of hydrotalcite-like layered compounds that have the special layered structure and surface characteristics as a new type of photocatalyst carrier to achieve the coupling synergistic effect of adsorption and photocatalytic degradation and fundamentally create the harmless treatment of pollutants.

In this paper, the hydrotalcite surface was first modified with butyl titanate, the supported MgAl-LDH composite photocatalyst (TiO₂/MgAl-LDH) were prepared by a simple wet-chemical method. The phase, composition, surface microstructure were analyzed by XRD, SEM and EDS. On that basis, degradation performances of composite photocatalyst were investigated by using the methyl orange dye as the degradation object. Meanwhile, the mechanism of action and support effect were discussed.

2. Experimental

2.1. Reagent and Instrument

Magnesium nitrate (Mg(NO₃)₂•6H₂O, AR), aluminum nitrate (Al(NO₃)₃•9H₂O, AR), anhydrous sodium carbonate (Na₂CO₃, AR), sodium hydroxide (NaOH, AR), anhydrous ethanol (CH₃CH₂OH, AR), triethanolamine (N(CH₂CH₂OH)₃, AR), butyl titanate (C₁₆H₃₆O₄Ti, AR), titanium dioxide powder (P25TiO₂, nano scale), methyl orange (sodium dimethylamino benzene sulfonate, 20 mg/L). All the chemicals were used without any further purification.

The surface microstructure and surface elements of samples were characterized by using SEM(JSM-7500F, JEOL), XRD (Y-2000) and EDS (NAROUSA). Analysis of the as-prepared photocatalyst was carried out at room temperature with a Y-2000 apparatus using Cu target(Dandong ray instrument Co., Ltd. China). The UV-Vis absorption spectra of samples was observed by TU-1900 UV-Vis spectrophotometer.

2.2. Preparation of MgAl-LDH Carrier

Nitrates of Mg and Al are dissolved in distilled water along with appropriate amount of sodium carbonate (Na₂CO₃) and aqueous solution is put in an autoclave, adjusting pH to 12 by sodium hydroxide (NaOH) solution. According to the literature [8], programmed to achieve 120 °C and solution was kept for 18 h at this temperature. MgAl-LDH particles are precipitated in the solution, autoclave was cooled to room temperature, and the obtained samples were filtered, washed with distilled water or ethanol, and dried for 24 h.

2.3. Preparation of Supported Composite Photocatalyst

Tetrabutyl titanate-ethanol-triethanolamine system sol is prepared according to the literature [9-10], the MgAl-LDH powder was mixed with ethanol and ultrasonically dispersed, then, the mixture was added to the as-prepared sol and stirred vigorously for 2 h, the precipitates were filtered and dried in drying oven, the obtained samples was surface modified MgAl-LDH. The TiO₂ photocatalyst powder was mixed with ethanol and ultrasonically dispersed, then, the modified MgAl-LDH was added to the mixture and stirred for 1 h, standing 12 h; the precipitates were filtered and dried. The obtained product was calcined to removing the organic substance at 500 °C for 3 h. The supported TiO₂/MgAl-LDH composites photocatalyst was obtained. In the same way, a series of different weight ratio TiO₂/MgAl-LDH composites photocatalyst were also as-prepared via the same method.

2.4. Photocatalytic Activity Test

The methyl orange (MO) was chosen as the simulated dye wastewater model to test the photocatalytic activity of the synthesized catalyst [11-12]. In a typical process, 200 mg composites photocatalyst was added into 50 mL MO solution by a 40 W ultraviolet light lamps (wavelength 2537 Å, distance 6 cm) with the magnetic stirring. After irradiation under different time period, taking the supernatant liquor, centrifuged and filtrated, the photocatalytic activity was tested by UV-vis spectrophotometer at 465 nm (the maximum absorption wavelength of methyl orange at 465 nm), the photocatalytic degradation rate (D) was calculated by the following formula: $D = (A_0 - A) / A_0 \times 100\%$. (Where A₀ and A denote the absorbance of the dye solution before and after photocatalytic treatment respectively).



3. Results and Discussion

3.1. Characterizations of the Materials

3.1.1. XRD Analysis

The phase structure and crystal form of different as-prepared samples are performed by X-ray diffraction. Fig. 1 shows the XRD patterns of the MgAl-LDH, MgAl-LDO and supported composite photocatalyst (TiO₂/MgAl-LDH). From Fig. 1a, the characteristic diffraction peaks of Mg-Al hydroxalcalite was appeared at the $2\theta = 11.30^\circ$, 23.06° , 34.66° , 38.98° , 46.51° and 60.61° (MgAl-LDH, PDF#22-700), this implies that the product was MgAl-LDH. Fig. 1c shows the XRD patterns of the product of MgAl-LDH calcined at 500 °C, compared with 1a, it is clearly observed that the characteristic peaks of the original hydroxalcalite layered compounds was disappeared, and the background of diffraction peak was higher, two new diffraction peaks appeared, the result showed that the product after calcination was magnesium aluminum composite oxide (MgAl-LDO). Fig. 1b shows the XRD patterns of the supported composite photocatalyst, the anatase and rutile TiO₂ diffraction peaks respectively appeared at $2\theta = 25.80$, 48.04 (Fig. 1b), it is indicated that TiO₂ were supported on the surface of MgAl-LDH particles with strongly bonded.

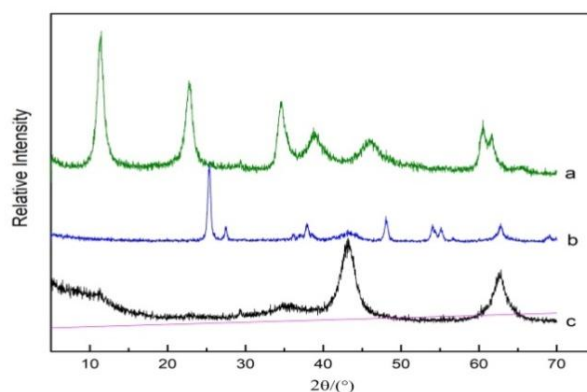


Figure 1: XRD spectra of samples (a: MgAl-LDH; b: TiO₂/MgAl-LDH; c: MgAl-LDO)

3.1.2. SEM and EDS Analysis

The surface microstructure of as-prepared samples was investigated by SEM. The MgAl-LDH morphology was shown in Fig. 2a, the MgAl-LDH prepared by the wet-chemical method is hexagonal and lamellar structure with good regularity, crystallinity, dispersion and homogeneity, the catalysts size was about 100-160 nm with uniform distribution (Fig. 2a). After calcination (Fig. 2b), we can see that the product (MgAl-LDO) still was lamellar structure, which regularity and homogeneity were inferior to MgAl-LDH. The supported composite photocatalyst TiO₂/MgAl-LDH morphology was shown in Fig. 2c, the TiO₂ particles were coated on the photocatalytic carrier surface, the TiO₂ particles size was about 20 nm with uniform distribution. It was further confirmed that the photocatalyst was well-loaded on the MgAl-LDO carrier surface with strongly bonded.

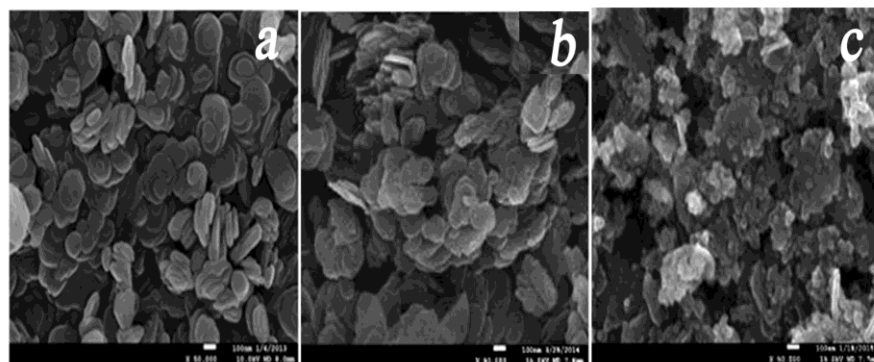


Figure 2: The image of samples (a: MgAl-LDH; b: MgAl-LDO; c: TiO₂/MgAl-LDH)



The chemical constituents of samples were revealed by EDS analysis. The typical spectra were shown in Fig. 3. The result show that raw MgAl-LDH mainly consisted of O, Mg and Al elements (Fig.3a), compared with Fig. 3b, it can be clearly seen increasing Ti element peak in the composite photocatalyst. The combined results of SEM, it was further confirmed that the photocatalyst was well-loaded on the MgAl-LDH particles surface by activation and modification process.

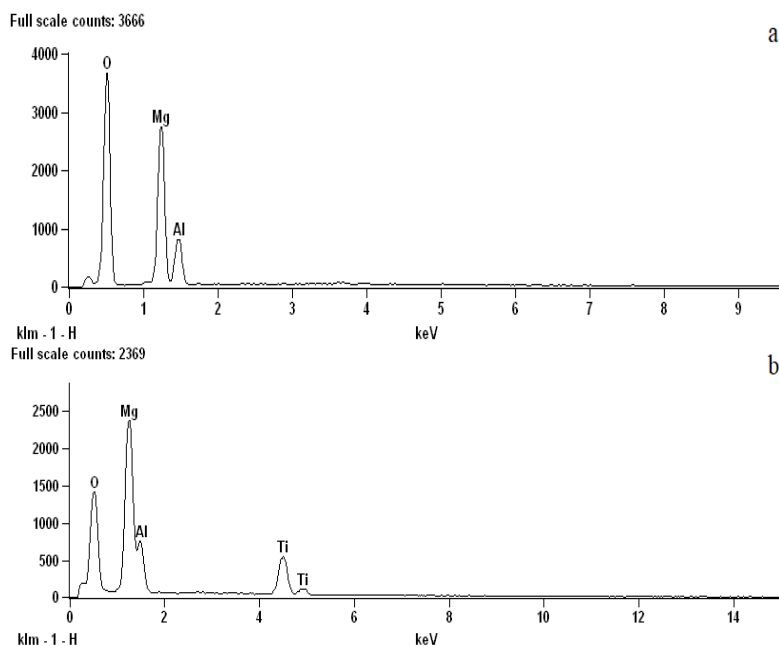


Figure 3: EDS spectrums of samples (a: raw MgAl-LDH;b: TiO₂/MgAl-LDH)

3.2. Photocatalytic Activity of Composite Photocatalyst

3.2.1. Effect of Loading Amount on Decolorization Rate

In order to evaluate photocatalytic activity of composite photocatalyst, some conditions were fixed with the 50 mL MO (20 mg/L) solution, system pH=3, 50 mg composite photocatalyst and 40W UV stable light irradiation for 90 min. The Fig. 4 show the photocatalytic activity at the different composition ratios (weight TiO₂: MgAl-LDO). It may be noted that the decolorization efficiency is about 58%, when have not TiO₂ photocatalyst. As can be seen from the curve, the decolorization rate was gradually increased with the TiO₂: MgAl-LDO ratio increasing, when the TiO₂: MgAl-LDO was 3:1, the decolorization rate reached more than 97%.

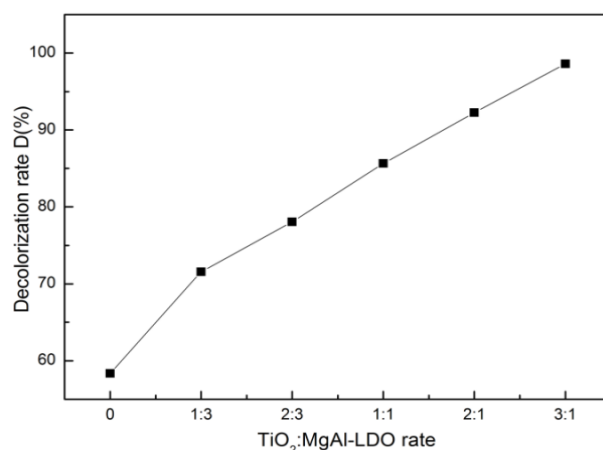


Figure 3: Effect of loading amount on decolorization rate

3.2.2. Effect of Catalyst Dosage on Decolorization Rate

The Fig. 5 show the photocatalytic activity at the different catalyst amounts (TiO₂: MgAl-LDO=1:1). From Fig. 5, the decolorization rate was gradually increased with the catalyst amount increasing other conditions remain same, when the catalyst amount was 60 mg; the decolorization rate reached more than 90%. However, further increasing the catalyst dosage resulting in a slight increase in the decolorization efficiency, the decolorization rate was stable.

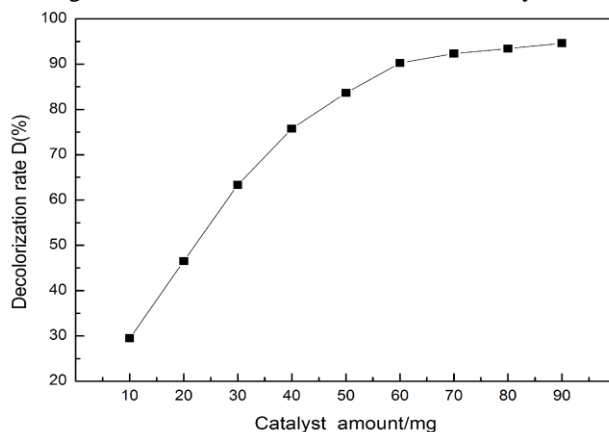


Figure 5: Effect of catalyst amount on decolorization rate

3.2.3. Effect of Photocatalytic Time on Decolorization Rate

The decolorization rate was showed in Fig. 6 at different photocatalytic time (compound catalyst dosage: 50 mg; TiO₂: MgAl-LDO=1:1). From Fig. 6, the decolorization rate was gradually increased with the photocatalytic time increasing. In addition, it's worth noting that the decolorization rate was obviously increased at the beginning. However, further increasing the photocatalytic time from 60 to 80 min resulting in a marginally increase in the decolorization efficiency. Subsequently, the decolorization rate reached maximum (91%) at 80min under UV radiation, with the increase of time, the decolorization rate was stable about 91%.

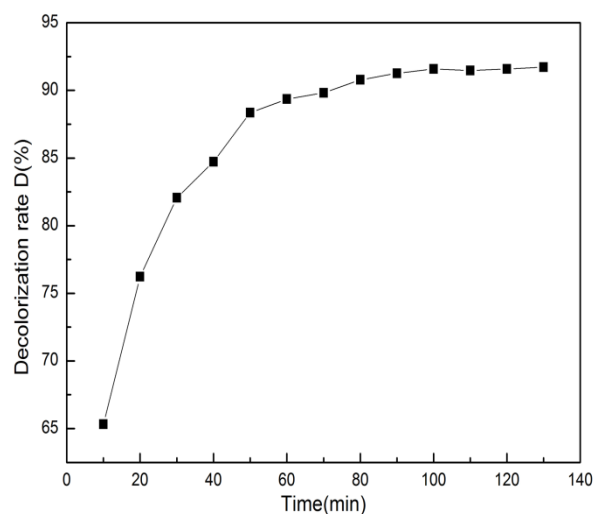


Figure 6: Effect of photocatalytic time on decolorization rate

3.2.4 Decolorization Mechanism of Composite Photocatalyst

TiO₂/MgAl-LDH supported composite photocatalyst had shown a special principle, the reason was attributed to the hydrotalcite has special layered structure. After calcination of MgAl-LDH, there were CO₃²⁻ and H₂O from the inter layer anions to be lost and the phase of MgAl-LDH transformation to magnesium aluminum oxide. The BET surface



area was measured, the result showed that the specific surface area of MgAl-LDO was 122.34 m²/g, which is larger than that of MgAl-LDH (23.202 m²/g).

At the beginning of the decolorization of the composite photocatalyst, the composite photocatalyst carrier was gradually recovered to the hydrotalcite original structure in the process of adsorbing the dye anions due to the calcined hydrotalcite has a structural "memory effect" and an inner layer anion exchange ability [13-16], the adsorption decolorization plays the leading role and the photocatalytic degradation of decolorization plays a minor role.

With photocatalytic time increasing, the TiO₂ plays the leading role after adsorption equilibrium. The carrier that unsupported photocatalyst shown higher decolorization rate when time of the photocatalytic and the amount of composite catalyst was fixed. The supported composite photocatalyst decolorization rate gradually increased with TiO₂ amount increasing.

In addition, the photocatalytic reaction is mainly carried out free radical reaction on the surface of the photocatalyst. Under the irradiation of UV lamp, the production and recombination of electron-hole pairs are directly influence related to the generation of H₂O₂, •OH, HO₂⁻ strong oxidized groups. The layered hydrotalcite carrier not only has a large specific surface area, but also hydroxyl groups on the layered plate can capture photo-generated holes, forming a bonded hydroxyl radical on the surface. This process suppressed the electron-hole pair recombination, beneficial to Induction of electron migration, can maximize the contact between the dye wastewater solution and the catalyst surface, and greatly enhance the active center and catalytic activity. So, the as-prepared TiO₂/MgAl-LDH composite photocatalyst showed the higher photocatalytic degradation efficiency.

However, the amount of the composite photocatalyst is not as much as possible and the excessive amount of the catalyst hinders the penetration and absorption of the ultraviolet rays. This can result in insufficient catalytic degradation performance of the photocatalyst.

Of course, supported photocatalyst prepared using hydrotalcite-like layered compounds also have their own disadvantages, such as agglomeration phenomenon, dispersivity problem and different anions have different exchange capacities. What's more, some cations on the layer may hinder electron-hole pairs, which not conducive to the formation of hydroxyl radicals. Ultimately reduces the catalytic performance. Therefore, the mechanism of coupled photocatalytic degradation needs further study.

4. Conclusions

- The MgAl-LDH prepared by the wet-chemical method is hexagonal and lamellar structure with good regularity, crystallinity, dispersion and homogeneity. Slight crystallization MgAl-LDO is made from MgAl-LDH by calcination, which regularity and homogeneity were inferior to MgAl-LDH, but the BET surface area is larger than that of MgAl-LDH (23.202 m²/g).
- The modified MgAl-LDH surface was avail to stable loading TiO₂ photocatalyst via sol process, and the TiO₂ were supported on the surface of particles with strongly bonded.
- The as-prepared MgAl-LDH carrier showed the higher adsorption efficiency. There are some factors have directly influence on the decolorization rate, such as supported amount, catalyst amount, and the time. Photocatalytic degradation of decolorization plays a leading role with the supported amount increasing. However, when the catalyst dosage and time reached certain level, further increasing the catalyst dosage and time resulting in a minor increase in the decolorization efficiency, the decolorization rate was stable.
- Adsorption plays a predominant role in the initial stage of decolorization, the TiO₂ plays the main role after adsorption equilibrium.

Acknowledgement

Mande Qiu, Mengli Shang, Yanlong Cui and Xu Bian declare that they have no conflict of interest. Many people have made invaluable contributions, both directly and indirectly to my research. I would like to express my warmest gratitude to them with valuable advice and access to the related resources on my thesis.



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