Effect of Co-solvent on the Performance of LDHs Photocatalytic Degradation of Methyl Orange Solution

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Abstract

In this paper, NiAlCe hydrotalcite was prepared by co-precipitation method and hydrothermal method in different volume fractions of ethylene glycol-water mixed solvent and polyethylene glycol-water mixed solvent, and the effect of photocatalytic degradation of methyl orange under ultraviolet light was studied. Samples were characterized by XRD, XPS, UV-Vis and FT-IR in order to find the reasons for the improvement of photocatalytic performance under co-solvent system. NiAlCe-10%EG(h) and NiAlCe-15%PEG(h) had smaller particle size, which was beneficial to photocatalytic performance. The degradation rate of methyl orange could reach up to 100% in 42 min using NiAlCe hydrotalcite with 10% volume fraction of EG and in 48 min using NiAlCe hydrotalcite with 15% volume fraction of PEG. The photocatalytic effect of NiAlCe hydrotalcite samples prepared by hydrothermal method were better than that prepared by co-precipitation method. This provided a new type of catalyst for the degradation of dyes: preparing with ethylene glycol-water mixed solvent.

Highlights

1. NiAlCe-LDHs was prepared in co-solvent systems.
2. NiAlCe-10%EG and NiAlCe-15%PEG had better photocatalytic degradation performance.
3. Hydrothermal method was better than co-precipitation method in MO degradation.

1 Introduction

Photocatalytic oxidation process can utilize the light energy to carry out the redox reaction and has broad application prospects in the field of wastewater treatment. It converts light energy into a chemical reaction to produce a catalysis that excites surrounding oxygen and water molecules into highly oxidizing free negative ions. However, the photocatalytic process still has problems such as low utilization rate of light energy and unsatisfactory photocatalytic effect. Therefore, how to improve the efficiency of the photocatalytic process is the focus of current research.

Layered double hydroxides (LDHs) are important inorganic crystal materials [1] with a sheet structure composed of divalent and trivalent metal cations. Due to its high specific surface area, good anion exchange capacity, expansion performance, low cost and environmental friendliness, it has attracted the attention of many researchers in the field of catalysis [2, 3], photocatalysis [4, 5], catalyst carrier [6], adsorbent [7, 8], composite material [2, 9], electrochemical reaction [10], medicine [11], etc. Since the divalent and trivalent metal cations could form an octahedral coordination structure with a hydroxide and oxygen in a variable ratio [12], hydrotalcite materials were used as photocatalysts to degrade organic wastewater [13], degrade pharmaceutical compounds [14], and oxidize and decompose NO$_x$ [15] and had achieved good photocatalytic effects.

Whether the layered structure of hydrotalcite was significant, as well as the regularity of shape, the uniformity of particle size distribution, and the dispersibility would have certain influence on its
application performance\cite{16}. It was an important way to improve the performance of LDHs by changing the preparation environment and then changing their structure. Yu et al.\cite{17,18} found that the Mg/Al hydrotalcite obtained using ethanol and EG as a co-solvent had high crystallinity and exhibited a regular hexagonal plate crystal form. The formation of hydrogen bonds had a significant effect on the microstructure and thermal properties of hydrotalcite during its synthesis\cite{19}.

In our previous work\cite{5}, NiAlCe-LDHs were prepared by co-precipitation method and exhibited good photocatalytic activities for methyl orange degradation. In this paper, ethylene glycol (EG) and polyethylene glycol (PEG) were used as important dispersants in the preparation and synthesis of NiAlCe-LDHs. A systematic study was carried out to optimize the amount of EG and PEG, and discuss the mechanism of photocatalytic performance improvement.

2 Experimental

2.1 Preparation of NiAlCe-LDHs

NiAlCe-LDHs with Ni\(^{2+}/(\text{Al}^{3+}+\text{Ce}^{3+})\) molar ratio of 3 was prepared by co-precipitation method at constant pH of 9.3 referred to previous literature\cite{5}. Certain amount of Ni(NO\(_3\))\(_2\)·6H\(_2\)O, Al(NO\(_3\))\(_3\)·9H\(_2\)O and Ce(NO\(_3\))\(_3\)·9H\(_2\)O were dissolved in 200mL deionized water, denoted as mixed salt solution A. NaOH and Na\(_2\)CO\(_3\) were dissolved in 150mL deionized water, denoted as mixed alkali solution B. Solution A and B were simultaneously added drop wise to a solution of 100mL deionized water in a four-necked flask with vigorous stirring, and then heated at 80°C. The resulting co-precipitation was aged at 60°C for 24h, then washed with distilled water for several times until neutral pH, and dried at 60°C for 24h to obtain NiAlCe-LDHs.

2.2 Preparation of NiAlCe-LDHs under co-solvent system

NiAlCe-LDHs with Ni\(^{2+}/(\text{Al}^{3+}+\text{Ce}^{3+})\) molar ratio of 3 was prepared by co-precipitation method under ethylene glycol (EG)-water co-solvent system and polyethylene glycol (PEG)-water co-solvent system, respectively. A co-solvent system with different volume fractions was configured. The weighed salt and the alkaline solution were separately dissolved in a 200 mL and 150 mL co-solvent system. The salt solution was recorded as A1 and the alkali solution was recorded as B1. Solution A1 and B1 were simultaneously added drop wise with vigorous stirring, and then heated at 80°C. The resulting co-precipitation was aged at 60°C for 24h, then washed with distilled water for several times until neutral pH, and dried at 60°C for 24h to obtain NiAlCe-EG(c) and NiAlCe-PEG(c).

NiAlCe-LDHs with Ni\(^{2+}/(\text{Al}^{3+}+\text{Ce}^{3+})\) molar ratio of 3 was also prepared by hydrothermal method under co-solvent systems. Solution A1 and B1 were placed in the reaction vessel and then the reaction kettle was placed in an oven at 60°C for 24 h. After that, the solution in the reaction kettle was filtered, washed and dried. The obtained materials were recorded as NiAlCe-EG(h) and NiAlCe-PEG(h).

2.3 Characterization
X-ray diffraction (XRD) was recorded in the 2θ range of 3–80° at a scan rate of 10°/min (step size 0.02°/s) on a RINT2000 vertical diffractometer with a Cu Kα radiation operated at 40kV and 150mA. X-ray photoelectron spectroscopy (XPS) was recorded on a XPS system (A1 K Alpha, \( h\nu = 1486.6 \) eV). The ultraviolet visible (UV-Vis) diffuse reflectance spectrum was carried out using a UV-Vis spectrometer (Lambda 950) at a wavelength range of 200-800nm by the standard Kubelka-Munk method. The structures of the LDHs were further analyzed by Fourier transformed infrared spectroscopy (FT-IR).

### 2.4 Photocatalytic experiment

The photocatalytic activity of NiAlCe-LDHs was evaluated for photocatalytic degradation of methyl orange (MO) with ultraviolet light irradiation using a 500W high pressure mercury lamp (as shown in Fig. 1). The photocatalytic reactor was a sandwich structure made of quartz glass, and the ultraviolet lamp tube was placed at the center of the inner tube. Cooling water was introduced into the quartz glass jacket. A layer of tin foil was wrapped around the quartz glass sleeve to isolate the external light source. 1 g catalyst was charged into the reactor, and MO solution (80 mg/L) was introduced into the quartz glass tube interlayer by a peristaltic pump to form a circulation system. The reaction system was circulated in the dark for 30–45 min to achieve adsorption equilibrium between the MO molecule and the catalyst surface. The reaction solution was taken every 10 min and centrifuged. The absorbance of the supernatant was measured at 463 nm using an ultraviolet-visible spectrophotometer.

In order to evaluate the photocatalytic performance of NiAlCe-LDHs, degradation rate were proposed as formula (1).

\[
\text{Degradation rate (\%)} = (1 - C / C_0) \times 100\% \quad (1)
\]

Where \( C_0 \) was the initial concentration of the MO solution and \( C \) was the constant concentration of the MO solution.

### 3 Results And Discussion

#### 3.1 Characterization of LDHs

Figure 2 showed the XRD patterns of NiAlCe-LDHs prepared under different conditions. The patterns at 11.50°, 23.41°, 34.54°, 39.11°, 60.28° and 62.11° were corresponded to (003), (006), (009), (015), (110) and (113), respectively, which indicated the existence of a multilayer hydrotalcite structure \cite{21-23}. The diffraction peaks appearing at 2θ=28.51°, 47.52° were corresponded to the hydrotalcite characteristic peaks of (111) and (220), indicating that a metal oxide containing Ni and Ce was produced \cite{24}. The XRD diffraction peaks of NiAlCe-LDHs prepared under co-solvent systems were relatively stronger and sharper, which means that the hydrotalcites contained more metal oxides of Ni and Ce. NiAl\(_2\)O\(_4\) can be determined by XRD patterns with the corresponding peak at about 18.98°, and CeO\(_2\) could be measured at about 56.24°. The peak at about 46.76° was inferred to be cerium carbide or cerium oxide, while the peak at about 31.78° represented alumina. The presence of NiAl\(_2\)O\(_4\), cerium carbide and cerium oxide would
affect the structure of the catalyst and might increase the activity of the photocatalyst. Compared with XRD pattern of NiAlCe-LDHs sample prepared using water as solvent, the diffraction peaks of NiAlCe-EG and NiAlCe-PEG samples prepared under co-solvent system were higher and sharper, which indicated the samples prepared under co-solvent system had stronger crystallinity \[25\].

Table 1 showed the average particle size and lattice parameters of NiAlCe-LDHs samples. The estimated error of the average particle size generally corresponded to ±0.5 nm. NiAlCe-10%EG(h) and NiAlCe-15%PEG(h) had smaller average particle size than those samples prepared by co-precipitation method. The basal spacing of each diffraction peak was calculated by the Bragg equation (2) as follows:

\[
2d\sin\theta = \lambda
\]

\[2\]

Where, \(d\) was the basal spacing, \(\theta\) was the angle between the incident X-ray and the corresponding crystal plane, and \(\lambda\) was the wavelength of the X-ray. \(d_{003}\) of all samples were around 0.79 nm, which was similar to the reported results of the (003) basal spacing of carbonate hydrotalcite \[26\]. \(d_{110}\) reflected the laminates density of the atomic arrangement. The larger the atomic arrangement laminates density was, the smaller the lattice parameter \(a\) was, as well as the smaller \(d_{110}\) was \[27\]. It could be seen from Table 1 that NiAlCe-10%EG(h) and NiAlCe-15%PEG(h) had larger laminates density of the atomic arrangement than other samples which was beneficial to its light utilization efficiency.

Table 1 Average particle size and lattice parameters of NiAlCe-LDHs samples

| Sample            | Average particle size / (nm) | \(d_{003}\) / (nm) | \(d_{110}\) / (nm) | \(a\) / (nm) |
|-------------------|-------------------------------|---------------------|---------------------|-------------|
| NiAlCe-10%EG(c)   | 31                            | 0.7936              | 0.1525              | 0.9541      |
| NiAlCe-10%EG(h)   | 19                            | 0.7964              | 0.1522              | 0.9483      |
| NiAlCe-15%PEG(c)  | 26                            | 0.7894              | 0.1532              | 0.9498      |
| NiAlCe-15%PEG(h)  | 25                            | 0.7908              | 0.1524              | 0.9499      |
| NiAlCe-LDHs       | 7                             | 0.7950              | 0.1530              | 1.0577      |

Figure 3 was the XPS spectrums of Ce3d of NiAlCe-EG(c) and NiAlCe-EG(h), respectively. In Figure 3(a), the XPS spectrum of Ce3d of NiAlCe-EG(c) contained the following four peaks: V (879.68), V1 (883.5), U (898.43), U1 (916), where the labeled peaks were associated with Ce 3d\(_{3/2}\) and Ce 3d\(_{5/2}\), respectively \[28\]. The peaks labeled V (879.68), U (898.43) were assigned to Ce\(^{3+}\), while the peaks labeled V1 (883.5), U1 (916), were assigned to Ce\(^{4+}\). Ce\(^{3+}\) and Ce\(^{4+}\) could coexist near the XPS binding energy region of Ce3d, which confirmed the coexistence of Ce\(^{3+}\) and Ce\(^{4+}\) in NiAlCe-EG(c) sample \[29\]. The ratio of Ce\(^{3+}/Ce^{4+}\) of NiAlCe-EG(c) sample was calculated to be 45% from the area of the XPS peaks. In Figure 3(b), the XPS spectrum of Ce3d of NiAlCe-EG(h) contained the following five peaks: V (880.13), V1 (885.03), U (899.45), U1 (903.31), U2 (916.27), where the peaks correspond to Ce 3d\(_{3/2}\) and Ce 3d\(_{5/2}\), respectively. The peaks
labeled V (880.13), U (899.45), U1 (903.31) were assigned to Ce\textsuperscript{3+}, while the peaks labeled V1 (885.03), U2 (916.27) were assigned to Ce\textsuperscript{4+}. The ratio of Ce\textsuperscript{3+}/Ce\textsuperscript{4+} of NiAlCe-EG(h) sample was calculated to be 55%.

Figure 4 was the XPS spectrums of Ce3d of NiAlCe-PEG(c) and NiAlCe-PEG(h), respectively. In Figure 4(a), the XPS spectrum of Ce 3d of NiAlCe-PEG(c) contained the following two peaks: V (878.52), U (898.43), corresponding to Ce 3d\textsubscript{3/2} and Ce 3d\textsubscript{5/2}, respectively. The peak labeled V (878.52) was assigned to Ce\textsuperscript{3+}, while the peak labeled U (898.43) was assigned to Ce\textsuperscript{4+}, and the ratio of Ce\textsuperscript{3+}/Ce\textsuperscript{4+} of NiAlCe-PEG(c) sample was calculated to be 38%. In Figure 4(b), the XPS spectrum of Ce 3d of NiAlCe-PEG(h) contained the following three peaks: V (878.49), U (897.24), U1 (916), corresponding to Ce3d\textsubscript{3/2} and Ce3d\textsubscript{5/2}, respectively. The peaks labeled V (878.49), U (897.24) belonged to Ce\textsuperscript{3+}, and the peak labeled U1 (916) assigned to Ce\textsuperscript{4+}. The Ce\textsuperscript{3+}/Ce\textsuperscript{4+} of NiAlCe-PEG(h) sample was calculated to be 43%.

Compared with NiAlCe-LDHs, the ratio of Ce\textsuperscript{3+}/Ce\textsuperscript{4+} of which was calculated to be 24%, NiAlCe-EG samples and NiAlCe-PEG samples had larger Ce\textsuperscript{3+}/Ce\textsuperscript{4+} values. NiAlCe-EG(h) and NiAlCe-PEG(h) samples had larger Ce\textsuperscript{3+}/Ce\textsuperscript{4+} values than that of NiAlCe-EG(c) and NiAlCe-PEG(c) samples. Ce\textsuperscript{3+} ions acted as hole traps, thereby delaying the recombination of photogenerated electrons and holes\cite{30}. Therefore, higher Ce\textsuperscript{3+}/Ce\textsuperscript{4+} value had better photocatalytic performance.

The UV-Vis spectra of NiAlCe-LDHs prepared under different conditions was shown in Figure 5. All NiAlCe-LDHs samples showed absorption bands around 280 nm and 630 nm, indicating that the samples exhibited absorption in the visible and the ultraviolet region. According to the relationship between absorbance (A) and incident photo energy (hv), as well as the linear relationship between (Ahv)\textsuperscript{1/2} and (hv), the band gap (E\textsubscript{g}) could be calculated\cite{31}. The results were shown in Table 2. It was known that the narrow band gap favored to strong photo adsorption of the photocatalyst to generate electron-hole pairs, which could promote the photocatalytic reactions. Compared with the samples prepared by the co-precipitation method, thoses prepared by the hydrothermal method had smaller band gaps, which indicated that NiAlCe-10%EG(h) had better photocatalytic effect.

Table 2 The band gap of NiAlCe-LDHs samples

| Samples          | E\textsubscript{g} (eV) |
|------------------|------------------------|
| NiAlCe-10%EG(c)  | 1.610                  |
| NiAlCe-10%EG(h)  | 1.298                  |
| NiAlCe-15%PEG(c) | 2.370                  |
| NiAlCe-15%PEG(h) | 2.222                  |
| NiAlCe-LDHs      | 1.717                  |
The FT-IR of NiAlCe-LDHs prepared under different conditions was shown in Figure 6. The absorption peak at 3200-3700 cm\(^{-1}\) represented the hydroxyl group between the LDHs sample laminated \[^{32, 33}\] . The absorption peaks around 638 cm\(^{-1}\) and 1384 cm\(^{-1}\) corresponded to the bending vibration and expansion of CO\(_3^{2-}\) in LDHs \[^{34, 35}\] . The addition of EG and PEG affected the synthesis of LDHs by affecting the hydrogen bonding in the LDHs synthesis system. The addition of both solvents increased the content of hydroxyl groups in the system. This caused the release temperature of the crystal water in the LDHs sample to increase, thereby affecting the dehydration of the hydroxyl groups on the base layer, and the temperature of the CO\(_3^{2-}\) releasing CO\(_2\) between the layers. The crystallization water with high hydration degree could be easily formed during the reaction process, thereby affecting the accumulation of the ordered structure of the hydrotalcite and the grain growth. But when EG was added too much, the role of hydration-hydrogen bonds was stronger. At this time, it was not conducive to the adjustment of the structure inside the hydrotalcite sample, reducing the regularity of LDHs.

### 3.2 Photocatalytic activity

Figure 7 showed the photocatalytic activity of NiAlCe-LDHs prepared under different conditions. As could be seen in Figure 7(a), the photocatalytic activity of NiAlCe-LDHs with 10% volume fraction of EG was significantly better than those with other volume fractions. The degradation rate of methyl orange could reach up to 100% in 42 min with NiAlCe-10%EG(c). NiAlCe-10%EG(h) sample showed better photocatalytic performance than NiAlCe-10%EG(c), which could degrade methyl orange in 36 min. As shown in Figure 7(b), the photocatalytic activity of NiAlCe-LDHs with 15% volume fraction of PEG was significantly better than those with other volume fractions. The degradation rate of methyl orange could reach up to 100% in 48 min with NiAlCe-15%PEG(c). Also, NiAlCe-15%PEG(h) sample showed better photocatalytic performance than NiAlCe-15%PEG(c), which could degrade methyl orange in 36 min.

### Conclusions

NiAlCe-LDHs prepared by co-precipitation method and hydrothermal method in different volume fractions of ethylene glycol-water mixed solvent and polyethylene glycol-water mixed solvent were used as photocatalysts for MO degradation under UV light. Co-solvent system affected the photocatalytic performance of hydrotalcite. The degradation rate of methyl orange could reach up to 100% in 42 min using NiAlCe-10%EG(c) and in 48 min using NiAlCe-15%PEG(c). The photocatalytic effect of NiAlCe hydrotalcite samples prepared by hydrothermal method were better than that prepared by co-precipitation method, because the former had larger laminates density of the atomic arrangement which was beneficial to its light utilization efficiency.

### Declarations

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Figures

Figure 1

Schematic diagram of photocatalytic device[20]
Figure 2

XRD patterns of NiAlCe-LDHs prepared under different conditions

Figure 3
XPS spectrum of Ce 3d of NiAlCe-EG(c) (a) and NiAlCe-EG(h) (b) 

Figure 4

XPS spectrum of Ce 3d of NiAlCe-PEG(c) (a) and NiAlCe-PEG(h) (b)

Figure 5

UV-Vis spectra of NiAlCe-LDHs prepared under different conditions
Figure 6

FT-IR spectra of NiAlCe-LDHs prepared under different conditions

Figure 7
Photocatalytic activity of NiAlCe-LDHs prepared under different conditions

Supplementary Files

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