Study on the Preparation of Zn-Doped NaA Molecular Sieve and Its Photocatalytic Performance

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Abstract. Zn-doped NaA molecular sieves were prepared by hydrothermal method using zinc nitrate, sodium metaaluminate, silica sol, etc. as raw materials. The samples were characterized by XRD, SEM, FT-IR, etc., using 300W xenon lamp as the light source. Rhodamine B (RhB) was used as the target degradant for photocatalytic experiments for its photocatalytic activity. The results showed that zinc ion doping increased the number of active sites on the NaA molecular sieve, effectively reduced the photoelectron-hole recombination probability in the molecular sieve, and improved the photocatalytic activity. The degradation rate of rhodamine B was 50.8% after 2 hours of light exposure, and its photocatalytic process complied with the Langmuir-Hinshelwood first-order kinetic equation.

Keywords. NaA molecular sieves; Zn-doping; photocatalysis; water treatment.

1. Introduction

Semiconductor photocatalysis, as a high-efficiency, low-cost, technology that can directly use renewable sunlight to generate chemical energy, also shows great potential in solving environmental problems [1,2]. The use of semiconductors such as TiO2, ZnO, and CuO as nanocatalysts is the most used photocatalyst today [3-6]. However, the photogenerated electrons and holes of such nanophotocatalysts are easy to recombine, which makes their quantum efficiency lower [7]. Specific surface area and reactive active sites are very important factors for effective catalytic degradation of organic matters. Nano-semiconductor catalysts can slow down the recombination rate of their electrons and holes by recombining or modifying with a carrier, and improve the photon efficiency [8, 9].

As an ideal catalyst carrier, molecular sieve has a basic structure with a negatively charged skeleton. It is composed of interlocking [SiO4] and [AlO4] tetrahedrons, which are connected together by a variety of regular arrangements through a common oxygen atom, resulting in high porosity and the gas has strong adsorption capacity [10]. The enrichment of surface electrons can suppress the electron-hole recombination while reducing the scattering of ultraviolet rays, and can form stable, molecular-sized nano-semiconductor clusters in the molecular sieve pore structure. It can solve the problem of difficult recovery and high cost of nano-semiconductor catalysts in the repeated experiments [11]. Doping Zn2+ into the NaA molecular sieve can utilize the ZnO structural unit to exert the photocatalytic effect, and at the same time cooperate with the Al-O structural unit to improve the catalytic effect. Meanwhile, with the help of the structural characteristics of the molecular sieve, it is in full contact with the catalyzed substance, which avoids the problem of agglomeration when used alone, and can improve the catalytic
efficiency. In our work, Zn-doped NaA molecular sieves was synthesized by hydrothermal method and its photocatalysis activity was systematically studied with rhodamine B as the target pollutant.

2. Materials and Methods

2.1. Materials
Zinc nitrate hexahydrate (Zn(NO$_3$)$_2$·6H$_2$O, CP), Sodium metaaluminate (NaAlO$_2$, CP) and silica sol (SiO$_2$, CP), were bought from Tianjin Guangfu Chemical Reagent Co. LTD. Sodium hydroxide (NaOH, AR) and Rhodamine B (RhB, AR) were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Catalyst Synthesis
Zn-doped NaA molecular sieves was synthesized using sodium metaaluminate as the aluminum source, silica sol as the silicon source, and zinc nitrate as the zinc source, adjusting the alkalinity with sodium hydroxide, according the molar ratio of Al$_2$O$_3$:SiO$_2$:Zn(NO$_3$)$_2$:Na$_2$O:H$_2$O=1:2:2: 80. First, silica sol was added to the dissolved zinc nitrate solution, then sodium metaaluminate solution was added into the solution with stirring. A pure white liquid was obtained after stirring mechanically at 30°C for 30 min in a water bath; then sealed with plastic wrap and transferred to a drying cabinet aging at 40°C for 48h; finally transferring it to a 100 mL polytetrafluoroethylene-lined hydrothermal kettle for at 120°C for 1h. Zn-doped NaA molecular sieve sample was obtained after removing the supernatant, washing with deionized water and absolute ethanol and drying for 4h.

2.3. Characterization
X-ray diffraction (XRD) patterns were tested by Bruker AXS D8 Advance X diffractometer employing Cu Ka radiation. The surface morphology of samples was observed with FEI Quanta250 field emission scanning electron microscope. FT-IR spectra was recorded by Nicolet 5700 spectrometer through the KBr pellet technique.

2.4. Photocatalytic Activity Experiments
Degradation of RhB of experiments were carried out under different conditions for measuring the activity of catalysts, respectively. In detail, 0.1 g of catalyst was added to 100 mL of RhB solution with an initial concentration of $10^{-5}$ mol/L, the pH of which was adjusted using diluent of HNO$_3$ or NaOH solution. Photocatalytic reaction was carried out with the lighting of 500W mercury lamp after the solution has reached adsorption equilibrium in the dark for 30 minutes. The reaction solution was sampled in a time interval, centrifugal separated, and then the absorbance of the supernatant at 553 nm was analyzed immediately, during all the reaction process. The degradation efficiency was computed by $D = C_t/C_0 = A_t/A_0$, where C is concentration and A is absorbance. The degradation rate of RhB was used to evaluate the activity of the photocatalyst. In the repeating experiments, the reaction solution was centrifuged to obtain a catalyst precipitate, which was used again after drying.

3. Results and Discussion

3.1. Catalyst Characterization
Figure 1 is X-ray diffraction pattern of Zn-doped NaA molecular sieve. It can be found from the figure that diffraction peaks appear at 7.2°, 10.2°, 12.5°, 16.1°, 21.7°, 23.9°, 27.1°, 29.9°, and 34.1°. The NaA molecular sieve diffraction peaks appearing in the doped NaA molecular sieve were consistent with the standard spectrum of the NaA molecular sieve in the standard library (JCPDS, No. 43-0142), and the corresponding crystal plane indices were (200), (220), (222), (420), (600), (622), (642), (644) and (664). It showed that the Zn-doped NaA molecular sieve maintained the original molecular sieve framework [12]. In addition to the NaA molecular sieve diffraction peaks, ZnO diffraction peaks appeared at 31.8°, 34.5°, 36.3°, 47.6°, and 56.7°, which were consistent with the structure of the ZnO standard spectrum (JCPDS, No. 36-1451) in the standard library, corresponding to the crystal plane index is (100) (002).
(101) (102) (110), which indicating that the Zn-doped NaA molecular sieve was prepared successfully.

**Figure 1.** XRD patterns of prepared samples.  **Figure 2.** SEM images of prepared samples.

The elemental composition of the sample determined by XRF was Na$_2$O: 14.4%; Al$_2$O$_3$: 28.4%; SiO$_2$: 38.3%; ZnO: 15.9%, and the silicon-aluminum ratio was greater than 1, which indicating that 9.9% of zinc replaced part of the aluminum framework, and Zn doped NaA molecular sieve was prepared successfully, the remaining 6% of zinc was adsorbed in the pore structure of molecular sieve in the form of ZnO, which indicating that zinc participated in the synthesis process of molecular sieve and formed a certain doping for NaA molecular sieve, which was different from ZnO in the XRD patterns. The SEM image of the sample is shown in figure 2. It can be observed from the picture that the Zn-doped NaA molecular sieve particles had a cubic structure, indicating that a small amount of Zn doping had not changed the overall morphology and structure of the NaA molecular sieve, and the crystal shape was regular and clear, the particle size distribution was uniform, the surface was smooth and average. The particle size was about 500 nm.

**Figure 3.** FT-IR pattern of prepared sample.

The chemical bond and functional group composition of Zn-doped NaA molecular sieve were investigated. It can be seen form figure 3, 466.2 cm$^{-1}$ was the bending vibration of the internal TO bond, 556.7 cm$^{-1}$ was the bending vibration of the double quaternary ring, and the 667 and 1008 cm$^{-1}$ were the symmetrical stretching vibration peaks of the internally connected [TO$_4$] tetrahedron. And antisymmetric stretching vibration peaks, the band about 1650 cm$^{-1}$ was the stretching vibration peak of HOH adsorbed on the surface, and the absorption peak of structural water at 3400 cm$^{-1}$ [13]. It can be seen from the figure that with the introducing of Zn, absorption peaks in NaA molecular sieve appeared
at 2900 and 1500 cm$^{-1}$, but the NaA molecular sieve was not absorbed in this area, and the introduction of zinc combined with part of -OH, reducing the content of adsorbed water and structured water on the surface of the molecular sieve made its peak decrease, indicating that heteroatoms have been entered into the frame of the molecular sieve and Zn-O-Si bonds was formed [14]. The surface of the prepared Zn doped NaA molecular sieve had rich hydroxyl functional groups, which was helpful for capturing photo-generated holes to form hydroxyl radicals with oxidative activity, which promoting the photocatalytic reaction.

3.2. Photocatalytic Activity

As shown in figures 4 and 5, the adsorption capacity of Zn doped NaA molecular sieve was obviously higher than that of ZnO when the solution reached adsorption-desorption equilibrium after 30 minutes of mechanical agitation in the dark, owing to the large specific surface area of the molecular sieve provides more adsorption sites for the dye. After visible light irradiation for 2h, the degradation rates of Rhodamine B by ZnO and Zn-doped NaA molecular sieves were 34.4% and 50.8%. The doping of Zn significantly improved the photocatalytic activity of the molecular sieve. On the one hand, it could effectively avoid the problem of nano-ZnO agglomeration and enlarged the effective contact area of the reaction; on the other hand, it could reduce the electron-hole recombination rate and improve the photocatalytic activity. The degradation rate of Rhodamine B by ZnO was about 35% after 4 hours of illumination, and the degradation efficiency of Rhodamine B by Zn-doped NaA molecular sieve was 50.8% after 2 hours of illumination. With the extension of light time, the degradation rate did not change significantly. Zn-doped NaA molecular sieves could effectively improve the photocatalytic performance under visible light conditions.

![Figure 4. Effect of different samples on the degradation rate of RhB.](image)

![Figure 5. Effect of the irradiation time on the degradation of RhB.](image)

In order to evaluate the photochemical stability of Zn-doped NaA molecular sieves under visible light conditions, three repeated photocatalytic degradation of organic matters experiments were performed. The results were shown in figure 6. The degradation rates of rhodamine B by the catalyst in three repeated experiments were 50.8%, 48.12% and 46.18%, respectively, and it showed good photochemical stability. In summary, Zn-doped NaA molecular sieves have good photocatalytic capacity and stability under visible light conditions, and have good application prospects.
3.3. Photocatalytic Kinetics Simulation

The photocatalytic degradation results were shown in figure 7, its photocatalytic degradation of rhodamine B process was consistent with Langmuir-Hinshelwood first-order kinetic reaction equation. It can be found from the figure that the degradation rate of rhodamine B by Zn-doped NaA molecular sieve under ultraviolet light conditions was $0.02195 \text{min}^{-1}$, and the degradation rate under visible light conditions is $0.01051 \text{min}^{-1}$. The molecular sieve had a large specific surface area, strong ion exchange ability, and a strong electric field strength in the pores. The surface electrons was enriched, which suppressed the electron-hole recombination and improved the separation effect of photogenerated electrons-photogenerated holes.

4. Conclusions

Zn-doped NaA molecular sieve was prepared by hydrothermal synthesis. XRD, SEM, XRF and FT-IR were used to characterize and analyze the samples. Zn entered the molecular sieve framework, Zn-doped NaA molecular sieve had a regular shape, uniform particle size distribution, and an average particle size of around 500 nm. Zn-doped NaA molecular sieve had good photocatalytic performance and chemical stability under visible light, and could be recycled repeatedly. The photocatalytic process of Zn-doped NaA molecular sieve for RhB conformed to Langmuir-Hinshelwood first-order kinetic equation. Rhodamine B was degraded effectively by Zn-doped NaA molecular sieve under visible light, which showed that the modified photon expanded the photoresponse range of NaA molecular sieve, broadened the application range of NaA molecular sieve in photocatalysis for controlling the pollution of organic matter in water.

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