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Synthesis and Photocatalytic Activity of Hierarchical Zn-ZSM-5 Structures

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Abstract: Hierarchical Zn-ZSM-5 photocatalyst structures were synthesized via a hydrothermal one-pot synthesis route using a double template. Activated attapulgite (Si-ATP) and zinc nitrate ($\text{Zn}(\text{NO}_3)_2$) precursors were used as silicon and zinc sources, respectively. The structural properties, morphology, photocatalytic activity and the texture properties of the synthesized Zn-ZSM-5 photocatalysts were investigated using X-ray diffraction (XRD), scanning electron microscope (SEM), diffracted ultraviolet–visible (UV–Vis) spectrometry (DRUV–Vis) and N_2 adsorption/desorption, respectively. It was found that the composites exhibit a typical MFI framework structure, a hexahedral twin structure and typical UV absorption peaks at 292 nm and 246 nm, when the Zn/Si mole ratio reaches its optimum value of 1:100. The hierarchical nanocrystals exhibit a similar Brunauer–Emmett–Teller surface area ($309 \text{ m}^2 \text{ g}^{-1}$) and a high mesopore ratio (37.47%) as compared to commercial zeolites. Sub-nano-sized zinc oxide (ZnO) particles with small size moieties were implanted and isolated in the silica matrices of micro-mesoporous zeolite, which had a significant photocatalytic activity and reusability of degrading methylene blue (MB) dyeing wastewater. Using a 500 W mercury lamp with the wavelength range from 185–500 nm operating during an illumination time of 30 min, the concentration of MB decreases significantly in the presence of Zn-ZSM-5 photocatalyst leading to a 95.56% of degradation, where the ratio still remained at 94.32% after six times of reuse.

Keywords: hierarchical structures; Zn-ZSM-5 photocatalyst; micro-mesoporous; methylene blue



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1. Introduction

Printing and dyeing wastewaters are a complex mixture of pollutants including some carcinogenic, teratogenic and mutagenic organic compounds derived from aromatic hydrocarbons and heterocyclic compounds. The pollutants are characterized by high chroma, high chemical oxygen demand (COD), high pH, high salinity, high hardness and low biodegradability [1,2]. Therefore, efficient methods for degrading printing and dyeing wastewater for safe disposal are urgently needed [3]. The technique of photocatalysis enables an efficient use of solar energy to degrade organic matter and has, therefore, attracted considerable research interest recently to be utilized for printing and dyeing wastewater degradation [4–6].

In this context, the semiconducting photocatalyst ZnO has become a major research target in the field of photocatalytic degradation of water pollutants, since it offers several advantages such as facile synthesis, good practicability, an environmentally-friendly nature and no secondary pollution [7–9]. Notwithstanding the efficient degradation rates reported in these publications, pristine ZnO possesses some setbacks such as a wide energy band-gap ($E_g = 3.37 \text{ eV}$) and limited spectral response to ultraviolet (UV) light. At the same time, it is also prone to photochemical corrosion. Moreover, ZnO particles can easily agglomerate, resulting in a low recovery rate and poor performance in industrial applications. To overcome such disadvantages of pristine ZnO, different approaches have been followed to increase the specific surface area and to generate more reaction sites to improve the

photocatalytic activity [10–12]. In recent years, considerable research efforts have been dedicated to ZnO composite materials [13]. ZnO has been successfully combined with graphene oxide [14], single-walled carbon nanotubes [15], fullerenes [16], Ag [17] and Pd [18], which has improved its photocatalytic activity to some extent. However, these composites are limited by high cost and complicated multi-step synthesis procedures. As a possible solution, hierarchical ZSM-5 zeolite structures are widely used as carriers of adsorbents and photocatalysts due to a high specific surface area, considerable volume of the micro-mesoporous pores, good structural stability and great capability for the separation and recovery of systems [19–22].

Chen et al. [23] successfully synthesized ZnO nanorods as a matrix to fabricate noble metal (Pt, Pd, and Ru)-supported ZnO photocatalysts by a liquid phase reduction method. It was shown that the incorporation of such noble metals significantly improves the photocatalytic performance of ZnO. Yang et al. [24] reported the synthesis of ZnO/stellerite composites via a direct deposition method, where the close combination and effective dispersion of ZnO and stellerite was achieved. The bandgap was reduced significantly in the composite and enhanced adsorption was obtained leading to improved photocatalytic performance. Zahra [25] et al. showed that ZnO nanoparticles can precipitate on the surface of ZSM-5 zeolite. The resulting ZSM-5/ZnO nanocomposites were further modified by silver nanoparticles of different quantities to investigate their photocatalytic efficiency. The investigation of different models describing the dye removal kinetics, a pseudo-second-order model was found to be most promising. This led to the conclusion that zeolite is an excellent carrier of ZnO. However, only few studies have been reported on the preparation of hierarchical Zn-ZSM-5 zeolite photocatalyst structures using double templating agents and a one-step crystallization hydrothermal method, to the best of the authors' knowledge. Furthermore, few reports exist regarding the investigation of the effect of the Zn/Si molar ratio on the framework and pore structure of these synthetic composites.

In this paper, Si-ATP and $\text{Zn}(\text{NO}_3)_2$ were used as precursor silicon and Zn sources, respectively, to prepare hierarchical Zn-ZSM-5 zeolite photocatalyst via a hydrothermal one-pot synthesis process using a double template. The crystal structure, morphology, pore structure and photocatalytic activity of the samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), diffracted ultraviolet–visible (UV–Vis) spectrometry (DRUV–Vis), and N_2 adsorption/desorption and pore size distribution analysis, respectively. The effects of the pore structure and Zn/Si ratio on the photocatalytic performance of the synthesized products were investigated, and further details about the photocatalytic mechanism could be revealed.

2. Results and Discussion

2.1. Characterization by X-ray Diffraction (XRD)

Figure 1 shows XRD patterns of samples with different Zn/Si ratio. Strong diffraction peaks appeared in sample a at $2\theta = 7.9^\circ, 8.8^\circ, 23.2^\circ, 23.9^\circ$ and 24.4° , which is consistent with the typical MFI framework of hierarchical ZSM-5 zeolite [26]. These peaks are preserved in samples b, c and d, indicating crystalline order of the zeolite framework. However, with the increase of the Zn/Si ratio, the characteristic peak intensities of the zeolite decrease gradually, which indicates that the addition of Zn led to slight degradation of the crystallinity of the zeolite framework. An abrupt change is noted for a Zn/Si ratio of 1:25, when the diffraction peaks of ZSM-5 zeolite disappear. Only the onset of very broad peaks appear near $20\text{--}30^\circ$ and 60° can be observed, which indicates that the addition of excessive Zn source hinders the crystallization of the MFI framework. In this case, the synthetic product is an amorphous crystal containing zinc. Figure 2 shows XRD patterns of samples with different Zn/Si ratio between 25–70° for further exploring the synthesis of zinc oxide in the product. Zn/Si ratios range from 1: 200 to 1: 50, and the XRD patterns of these zeolites are in good agreement with the database JCPDS card (No.36-1451), $2\theta = 30.9^\circ, 34.4^\circ, 36.2^\circ, 47.5^\circ, 56.5^\circ, 62.8^\circ$ and 67.9° represents the crystal face (100) (002) (101) (102) (110) (103) and

(112) from hexahedron phase, respectively. With Zn/Si ratio increased to 1:100, the XRD pattern shows the characteristic peak intensity of ZnO is higher and sharper. The addition of excessive zinc source results in the disappearance of typical characteristic peaks of ZnO, which indicates that the crystal gradually becomes amorphous.

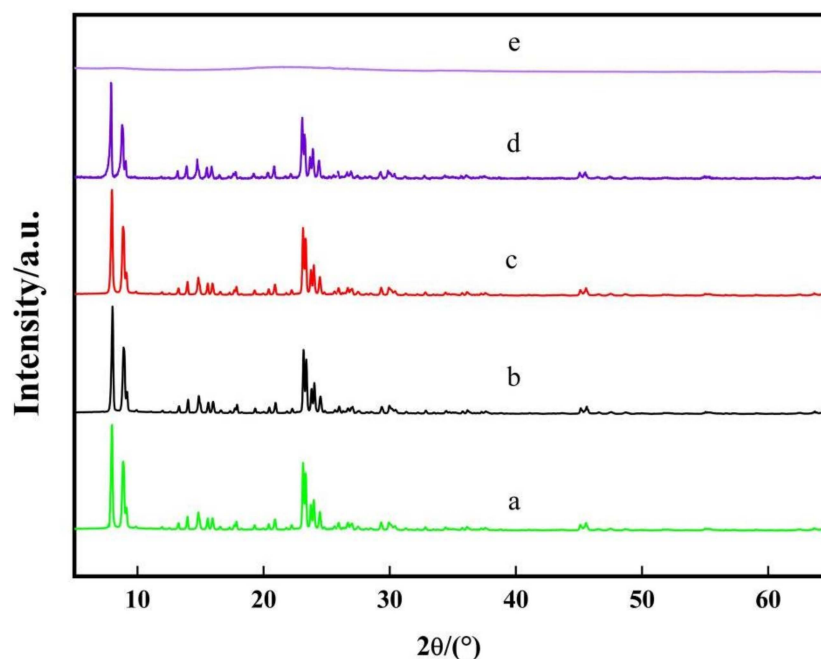


Figure 1. X-ray diffraction (XRD) patterns of pure ZSM-5 (a) and composite products with different Zn/Si ratios Zn-ZSM-5 n(Zn)/n(Si) of: (b) 1:200; (c) 1:100; (d) 1:50; (e) 1:25.

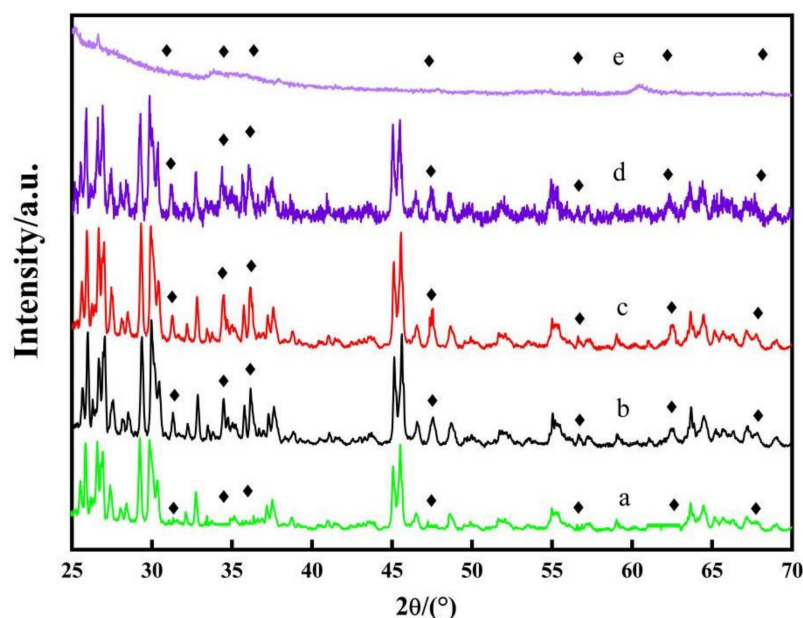


Figure 2. XRD (25–70°) patterns of pure ZSM-5 (a) and composite products with different Zn/Si ratios Zn-ZSM-5 n(Zn)/n(Si) of: (b) 1:200; (c) 1:100; (d) 1:50; (e) 1:25.

2.2. Characterization by Scanning Electron Microscopy (SEM)

SEM images collected with a $\times 10,000$ magnification depict the sample morphology with different Zn/Si ratios (Figure 3). Obviously, sample a is a typical hexahedral ZSM-5 zeolite. When the Zn content is increased in terms of a Zn/Si ratio in the range of 1:200 to 1:50, samples b, c, and d show hexagonal twinned grains. Two hexahedrons grow

vertically and alternately, forming a plurality of faces. In addition, with the change of the Zn/Si ratio, the grain size also changes. This may be attributed to the fact that the electronegativity of Zn^{2+} in the zeolite pore structure is stronger than that of the bridging oxygen on the aluminum in the main zeolite framework [26]. This may result in a clustering phenomenon between the crystals, accompanied by an unclear angular structure of the grains. At the same time, irregular grains are formed on the twin surface, which were identified as small sub-nano ZnO clusters using UV diffuse reflectance spectroscopy. On the other hand, sample e is flocculent and amorphous, and contains a considerable amount of impurities, indicating that the addition of excessive zinc would impede the growth of the hexahedron crystalline structure of zeolite ZSM-5.

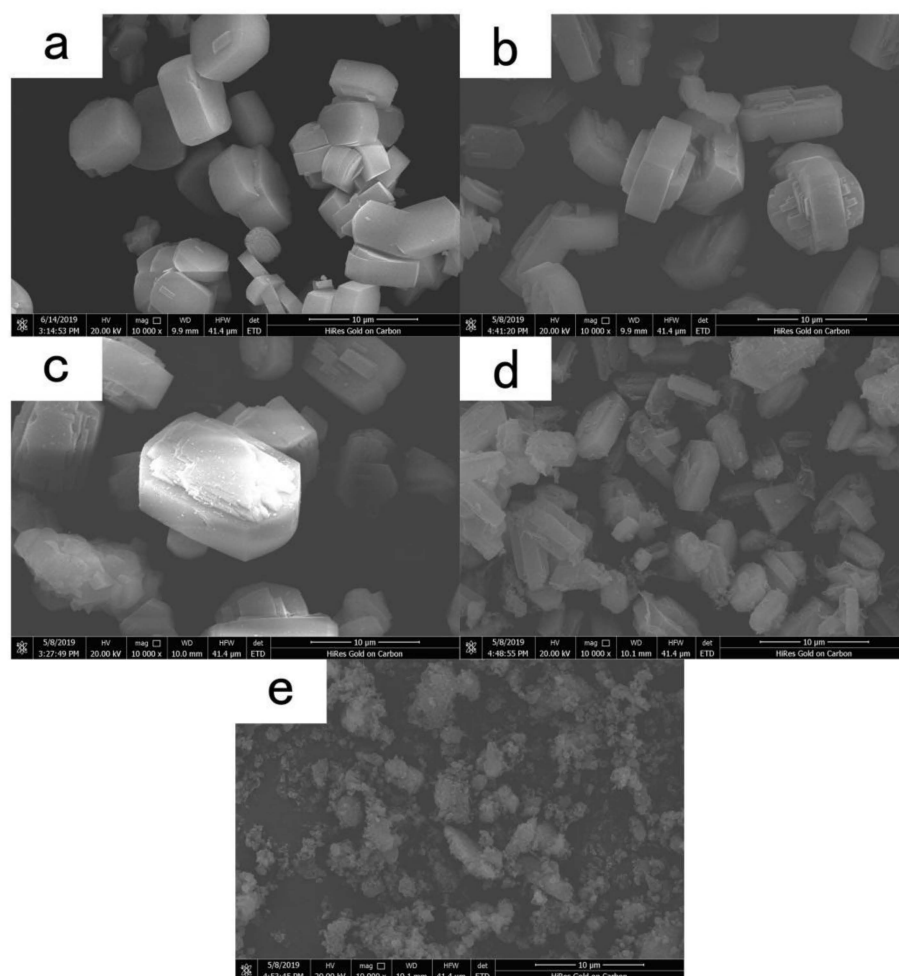


Figure 3. SEM morphology of pure ZSM-5 (a) and composite products with different Zn/Si ratios Zn-ZSM-5 $n(\text{Zn})/n(\text{Si})$ of: (b) 1:200; (c) 1:100; (d) 1:50; (e) 1:25.

2.3. Diffracted Ultraviolet–Visible (UV–Vis) Spectra

The diffuse reflectance UV–visible spectra demonstrate the photo-response activity of the photocatalysts with different Zn/Si ratios, as shown in Figure 4. When the Zn/Si ratio is within the range of 1:200 to 1:50, Zn species may be highly dispersed in the ZSM-5 zeolite framework, since they display absorption peaks at 292 nm and 246 nm. The absorption peak near 292 nm may be attributed to the small sub-nano ZnO clusters, and the absorption peak at 246 nm may be attributed to the characteristic peak of strong interaction between the small sub-nano ZnO cluster and zeolite [27]. For less Zn content in terms of a of Zn/Si ratio of 1:200 in sample b, the content of small sub-nano ZnO clusters in the sample b may be low. This in turn may lead to a quantum size effect, and concomitantly a peak blue-shifting at 246 nm is observed. When the Zn content increases to a Zn/Si ratio of

1:100, the intensity of the absorption peak increases significantly and red shifts can be detected, indicating that the sample now exhibits an expanded response range to light and the photocatalytic activity increases. When the Zn content further increases to a Zn/Si ratio of 1:50, the overlap of electronic wave functions is enlarged due to the formation of more sub-nano ZnO clusters, which may result in the increase of internal stress in the particles. Therefore, the energy band gap is narrowed. As a result, the UV absorption peak of the sample d is decreased and blue shifts were observed. According to the XRD and SEM results, an excessive Zn content may impede the formation of the main zeolite structure, leading to the appearance of amorphous crystals, and more importantly there are no groups or products with UV absorption activity present in the structure. For the determination of the bandgap value of the composite products with different Zn/Si ratios Zn-ZSM-5, the Tauc's method fitted with the data, the values of the band gap energy were that 3.36 eV, which was determined as for a neat semiconductor with ZnO from Figure 5.

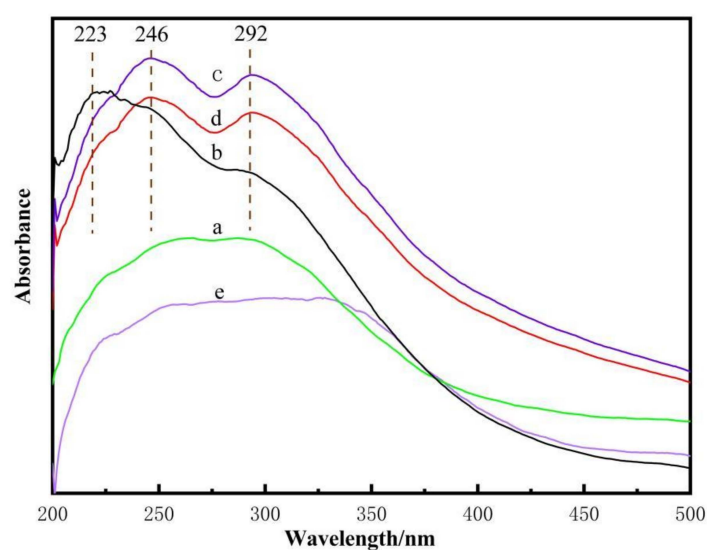


Figure 4. Diffuse reflectance ultraviolet–visible (UV–Vis) spectra of pure ZSM-5 (a) and composite products with different Zn/Si ratios Zn-ZSM-5 n(Zn)/n(Si) of: (b) 1:200; (c) 1:100; (d) 1:50; (e) 1:25.

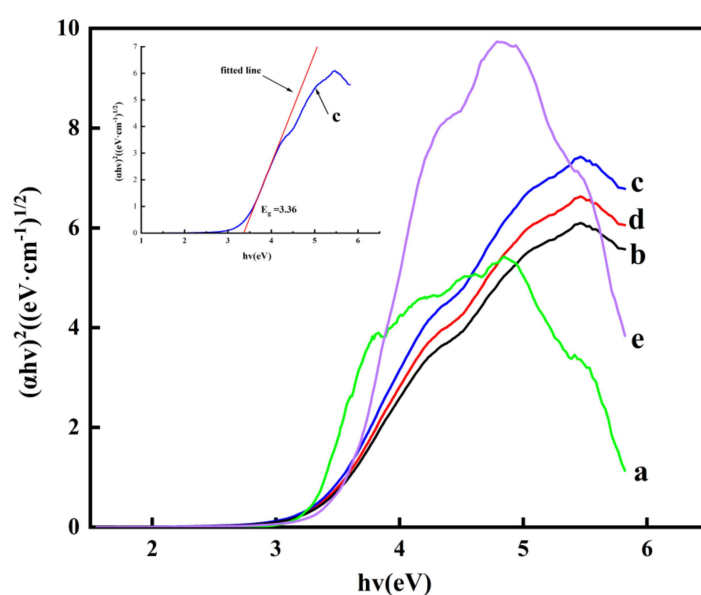


Figure 5. Tauc plots of pure ZSM-5 (a) and composite products with different Zn/Si ratios Zn-ZSM5 n(Zn)/n(Si) of: (b) 1:200; (c) 1:100; (d) 1:50; (e) 1:25. The determinations of E_g for measurements c are shown as insets.

2.4. Specific Surface Area and Pore Size

Figure 6 shows the N_2 adsorption–desorption isotherms of pure ZSM-5 and various composites with different Zn/Si ratios. H4-type hysteresis loops were observed in samples a–d, indicating that the mesoporous channels were uniform upon the addition of Zn to a certain extent, and the curves can be classified as type IV adsorption/desorption isotherms [28,29]. In the case of Zn excess, H3-type hysteresis loops appear in sample e, indicating that the shape and size of the channels have become uneven, which confirms that excessive Zn doping affects the crystal formation. Figure 7 shows the pore size distribution of hierarchical zeolite with different Zn contents. It can be seen from Table 1 that the pore structure and specific surface area change with the increase of the Zn content. For a Zn/Si ratio in the range from 1:200 to 1:50, the small sub-nano ZnO clusters affect the pore structure and especially the decrease of small-sized pores is significant. Furthermore, with the increase of the Zn content, the specific surface area shows a significant downward trend, which further demonstrates that sub-nano ZnO clusters with photocatalytic activity enter the surface and pores of the hierarchical zeolite. The pore size of 3.48 nm for pure ZSM-5 zeolite decreased to 2.26 nm with the introduction of Zn at a Zn/Si ratio of 1:100. This may be explained by the filling of the pores in the zeolite structure by sub-nanometer ZnO. When the Zn content continues to increase from a Zn/Si ratio of 1:100 to 1:50, the changes of specific surface area and pore size are no longer significant. This indicates that a Zn/Si ratio of 1:100 leads to a good pore structure and structural stability. When more Zn is added ($n(\text{Zn})/n(\text{Si}) > 1:50$), the excessive Zn will affect the formation of the zeolite framework as mentioned above, and the number of intergranular pores and macropores increase. The specific surface area drops suddenly and the total pore volume increases, which may be related to the fact that the original zeolite structure is no longer stable. Hierarchical ZSM-5 zeolite has good adsorption performance, which is beneficial to the enrichment of photocatalytic fillers entering the mesoporous zeolite. When the position of photocatalytic active groups is in the environment with relatively high substrate concentration, the photocatalytic reaction rate can be improved. Therefore, zeolite loses its stable structure when the material loses its structural stability.

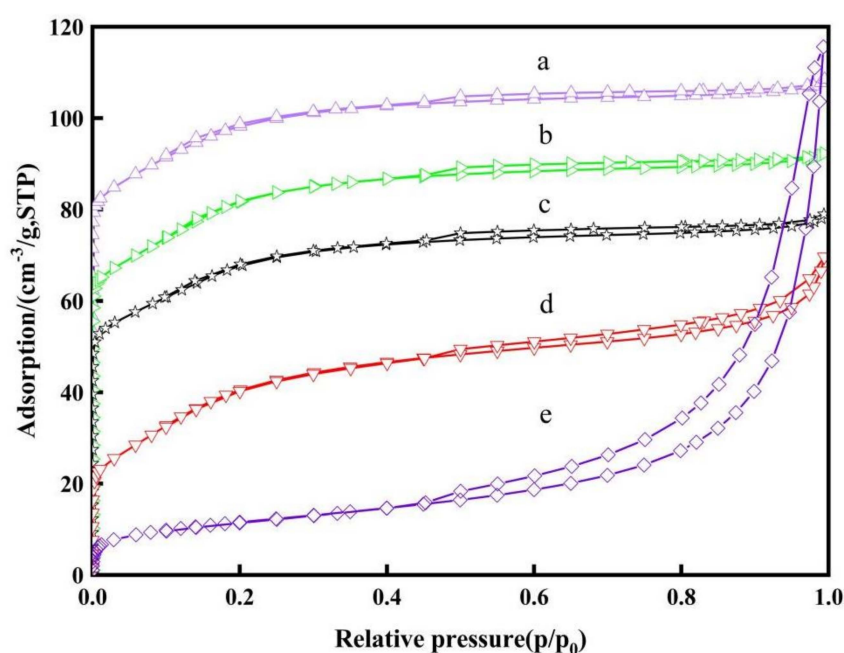


Figure 6. N_2 adsorption–desorption isotherms of pure ZSM-5 (a) and composite products with different Zn/Si ratios Zn–ZSM-5 $n(\text{Zn})/n(\text{Si})$ of: (b) 1:200; (c) 1:100; (d) 1:50; (e) 1:25.

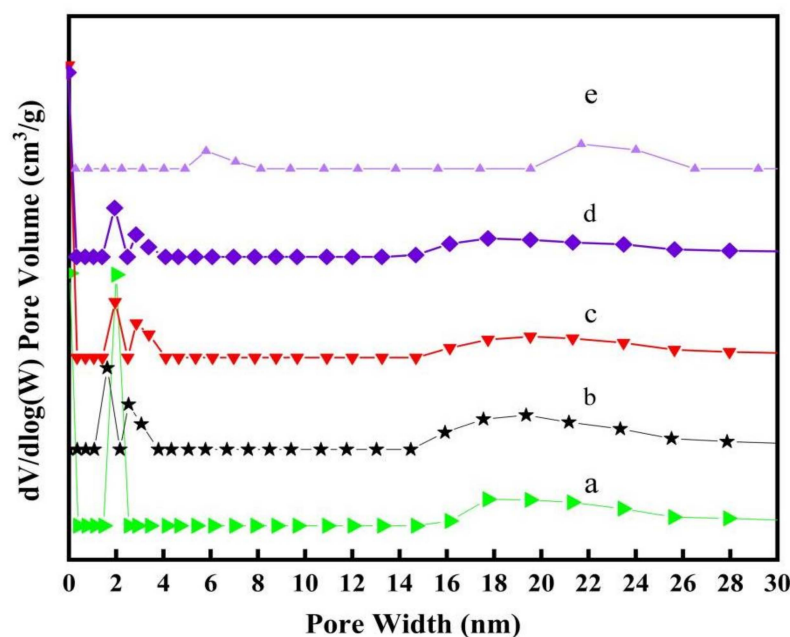


Figure 7. Pore size distribution of pure ZSM-5 (a) and composite products with different Zn/Si ratios Zn-ZSM-5 n(Zn)/n(Si) of: (b) 1:200; (c) 1:100; (d) 1:50; (e) 1:25.

Table 1. Textural properties of ZSM-5 and products with different Zn/Si ratios.

Sample	$S_{BET}/(m^2/g)$	$V_{tot}/(cm^3/g)$	$V_{mes}/(cm^3/g)$	V_{mes}/V_{tot} (%)	Pore Size/(nm)
a	333	0.19	0.093	48.83	3.48
b	319	0.18	0.072	39.67	2.73
c	309	0.18	0.068	37.47	2.46
d	308	0.16	0.055	33.41	2.26
e	120	0.54	0.497	91.78	14.46

3. Photocatalytic Performance

3.1. Photocatalytic Performances of Samples with Different Zn/Si Ratios

For the study of photocatalytic performance, the hierarchical Zn-ZSM-5 zeolite photocatalysts with different Zn/Si ratio were added to the MB solutions to perform photocatalytic reactions. The results are shown in Figure 8. In the dark reaction stage of 0–30 min, all samples were in the adsorption stage. After 30–60 min, the adsorption equilibrium state is reached. Under illumination for 0–10 min, the degradation rate curve showed a sharp decrease, followed by a gradual line flattening. For a Zn/Si ratio between 1:200 and 1:100, the photocatalytic degradation efficiency is significantly improved, while the photocatalytic degradation efficiency decreases when the ratio of Zn/Si is between 1:100 to 1:50. This implies that the optimal Zn/Si ratio is achieved at 1:100 in sample c. When the Zn content further increases to a Zn/Si ratio of 1:25 in sample e, the photocatalytic degradation efficiency was lower than that of the unmodified ZSM-5 zeolite. This is due to the instability of the zeolite structure as mentioned above. To summarize, in the case that the amount of Zn added is insufficient, the quantity of photocatalytic reaction sites determines the reaction rate. That is to say, the more Zn that is added, the better the photocatalytic performance of hierarchical Zn-containing zeolite will be. On the other hand, when Zn is added in excess, too many sub-nanometer ZnO clusters will affect the stability of the ZSM-5 zeolite framework structure and the synthesis of hierarchical Zn-containing zeolite basically fails and the structure cannot be used as a photocatalyst. The extra sub-nanometer ZnO clusters of sub- $NaNO_2$ may enter the pores and occupy the adsorption channel of MB, thus affecting the adsorption process. Additionally, the occupation of pores will also

affect the entry of dye molecules and the discharge of reaction intermediates, thus affecting the whole reaction process. Therefore, the deterioration of the photocatalytic activity, since the photocatalytic reactions take place on the surface of sub-nano ZnO clusters within the mesopores. Photocatalytic reactions will take place on the surface of sub-nano ZnO clusters with photocatalytic activity. An appropriate amount of Zn will increase the number of reactive groups without causing pore blockage and significant improvements in photocatalytic degradation can be achieved.

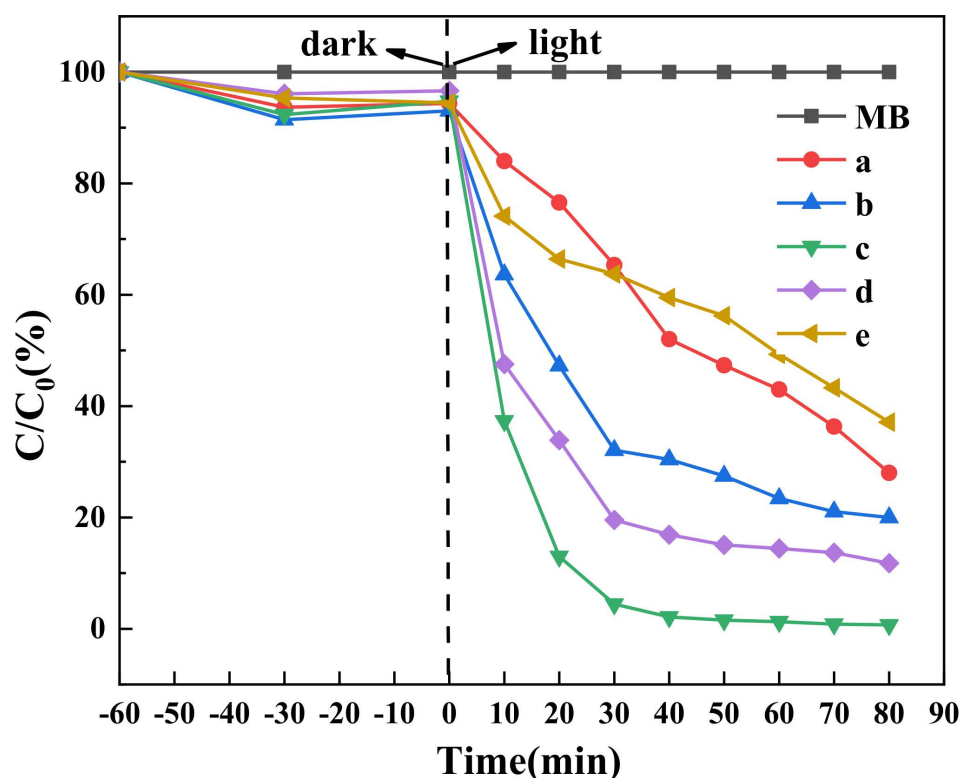


Figure 8. Photocatalytic effect of pure ZSM-5 (a) and composite products with different Zn/Si ratios Zn-ZSM-5 n(Zn)/n(Si) of: (b) 1:200; (c) 1:100; (d) 1:50; (e) 1:25. Experimental condition: V = 100 mL, T = 5 °C; catalyst dose, 0.2 g/L; initial concentration of pollutant, 50 mg/L; initial concentration of oxidant = 0.8 mmol/L; pH = 7.

3.2. Effects of Solution System on Photocatalytic Degradation

For Figure 9, under the illumination of 60 min, the photocatalytic degradation rate of the hierarchical Zn-ZSM-5 zeolite was 63.26%, and the hierarchical ZSM-5 zeolite with 0.1 mL of 30% (mass fraction) H₂O₂ solution is 61.44%. Meanwhile, after turning on the light, the reaction rate of dropping H₂O₂ solution is basically unaffected. This is because H₂O₂, as an electron trapping agent, can inhibit the recombination of photogenerated electron-hole pairs. Hydroxyl radical ($\cdot$ OH) was generated through a series of reactions after captured electrons by H₂O₂. The obtained $\cdot$ OH are well dispersed in the photocatalytic system, so that photocatalytic degradation of MB solution could be continuously performed. In addition, the bond energy of oxygen–oxygen bonds in H₂O₂ is 142 kJ/mol. When the wavelength of light source is less than 800 nm, the light utilization efficiency increases and more hydroxyl groups are generated.

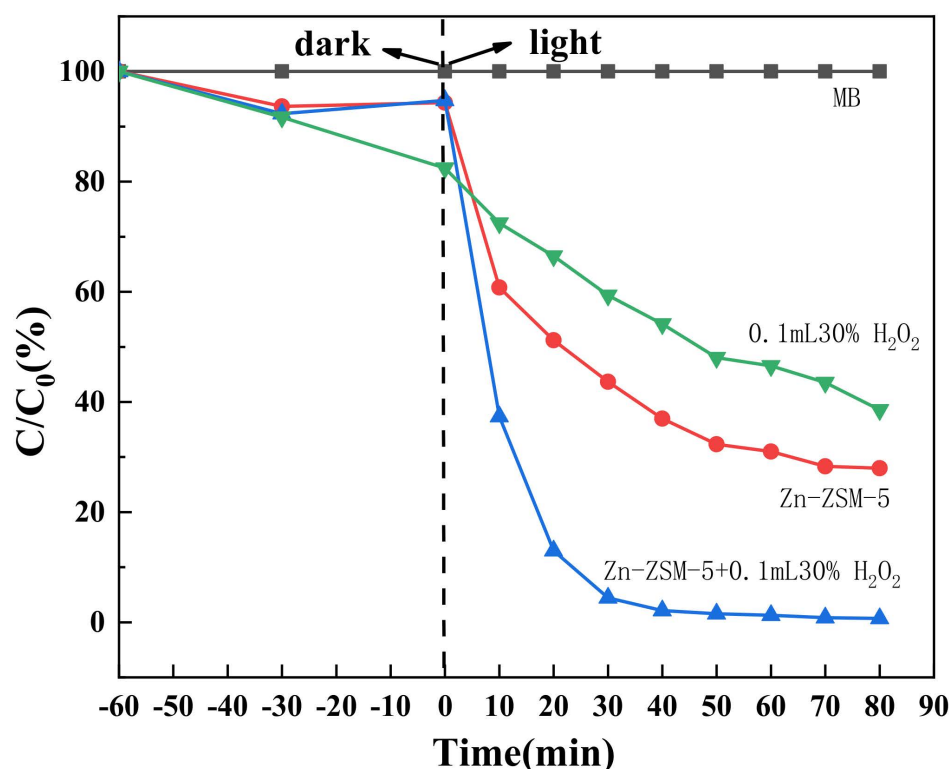


Figure 9. Effect of solution system on photocatalytic activity.

3.3. Photodegradation Kinetics of Hierarchical Zn-ZSM-5 Photocatalyst Structures

Under UV–visible light, the photodegradation kinetics of hierarchical Zn-ZSM-5 photocatalyst structures with different ratio of Zn/Si, $n(\text{Zn})/n(\text{Si})$ of: (b) 1:200; (c) 1:100; (d) 1:50, are described by pseudo-first order rate constant (Equation (1)), which illustrates that the reactions take place at a solid–liquid interface.

$$\ln(C/C_0) = -k \cdot t \quad (1)$$

In here, k is the apparent first-order rate constant for the MB degradation. Figure 10 shows the plot of natural logarithm of the normalized concentration $[\ln(C/C_0)]$ as a function of irradiation time (t) for the photodegradation of MB in the presence of hierarchical Zn-ZSM-5 photocatalyst structures. As can be seen in Figures 10 and 11, all the data fitted well to a straight line passing through the origin. The linear relationship suggests that the degradation reaction is pseudo-first-order. The obtained first-order rate constants (k) for the degradation of MB in the presence of hierarchical Zn-ZSM-5 photocatalyst structures with 1:100 ratio of Zn/Si had the fastest kinetics. Our kinetic results indicate that hierarchical Zn-ZSM-5 photocatalyst structures with 1:100 ratio of Zn/Si have a fast degradation rate of MB and show perfect photocatalytic performance. Therefore, apart from being a sorbent and a supporting platform, ZSM-5 also enhances the photocatalytic properties of ZnO. This excellent photocatalytic activity can be explained by two main processes: (1) direct adsorption of MB onto micro-mesoporous Zn-ZSM-5 zeolite, and (2) photodegradation of the adsorbed dye on the catalytic surface of Zn-ZSM-5 zeolite under UV-irradiation. The photocatalytic degradation can be enhanced by increasing the amount of dye adsorbed onto the adsorbent. Based on the above, the role of Zn-ZSM-5 zeolite is imperative in photocatalytic degradation due to its porous structure and high surface area, which provides more accessible adsorption sites. A control experiment for the photodegradation of MB (10 mg/L, 10 mL) by Zn-ZSM-5 zeolite (10 mg) is also conducted. However, no appreciable change in absorbance of the MB solution is observed even after 12 h. Zn-ZSM-5 zeolite has significantly high specific surface area, porosity and particle size as compared to traditional microporous ZSM-5 zeolite, which therefore lead to ZnO dispersion and

high MB adsorption. The importance of the adsorption step to photocatalysis is further revealed in this result. During the photocatalytic degradation, the color of MB solution disappeared as the solution exposed to UV light, which can be ascribed to the destruction of the chromophore.

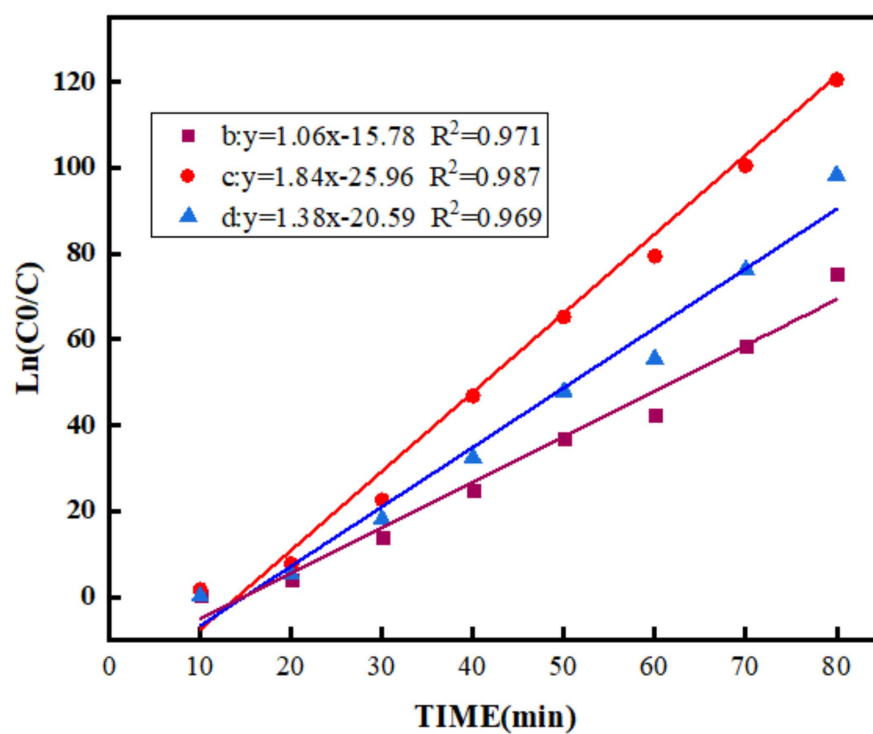


Figure 10. First-order kinetics of hierarchical Zn-ZSM-5 photocatalyst structures with different Zn/Si ratios Zn-ZSM-5 n(Zn)/n(Si) of: (b) 1:200; (c) 1:100; (d) 1:50.

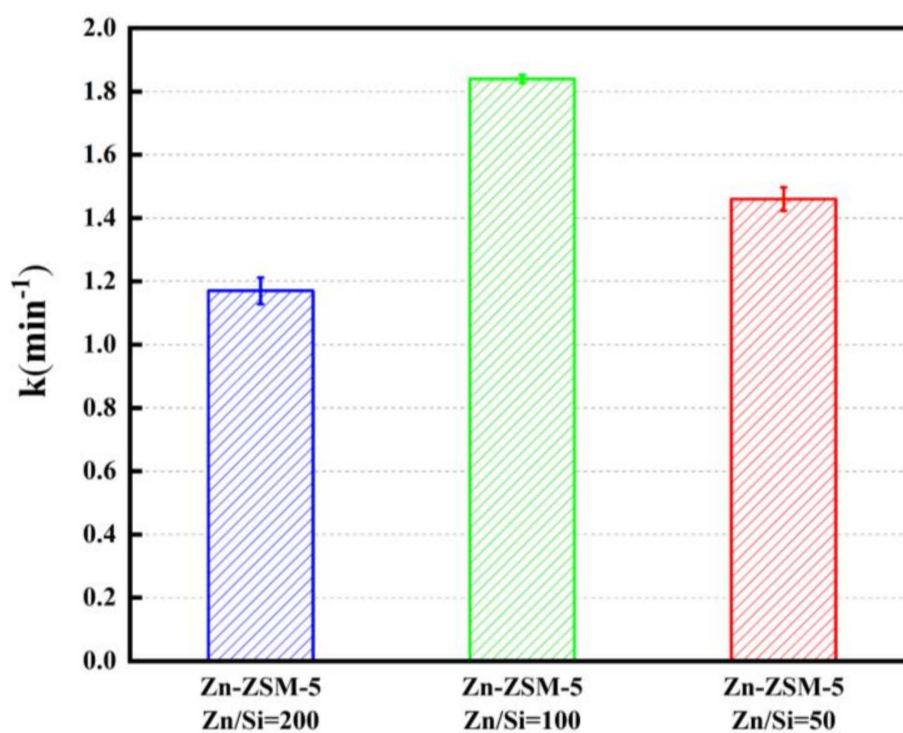


Figure 11. Photocatalysis kinetic constants of the evaluated conditions.

3.4. Reusability

In order to test the reusability of the material further, the recycling experiments are conducted under the same conditions, the result showed in Figure 12. The photocatalytic activity of hierarchical Zn-ZSM-5 (Zn/Si = 1:100) still reaches 94.32% after being reused for 6 times. Due to their morphology, some particles may not be recovered by suffering from the repeated mechanical external forces such as stirring, suction filtration and calcination, which may lead to the observed slight decrease of the photocatalytic performance of the zeolite after repeated operations. It should be stated though that the repeated use has only a moderate impact on the material. Under 500 W light irradiation, the optimal Zn-ZSM-5 zeolite (Zn/Si ratio = 1:100) exhibits a photocatalytic degradation rate of MB of 95.56% and 99.28% after 30 min and at the end of the reaction, respectively. In addition, the Zn-ZSM-5 zeolite photocatalyst has excellent photocatalytic stability and, more important the degradation rate after six cycles still exhibited a high value of 94.32%.

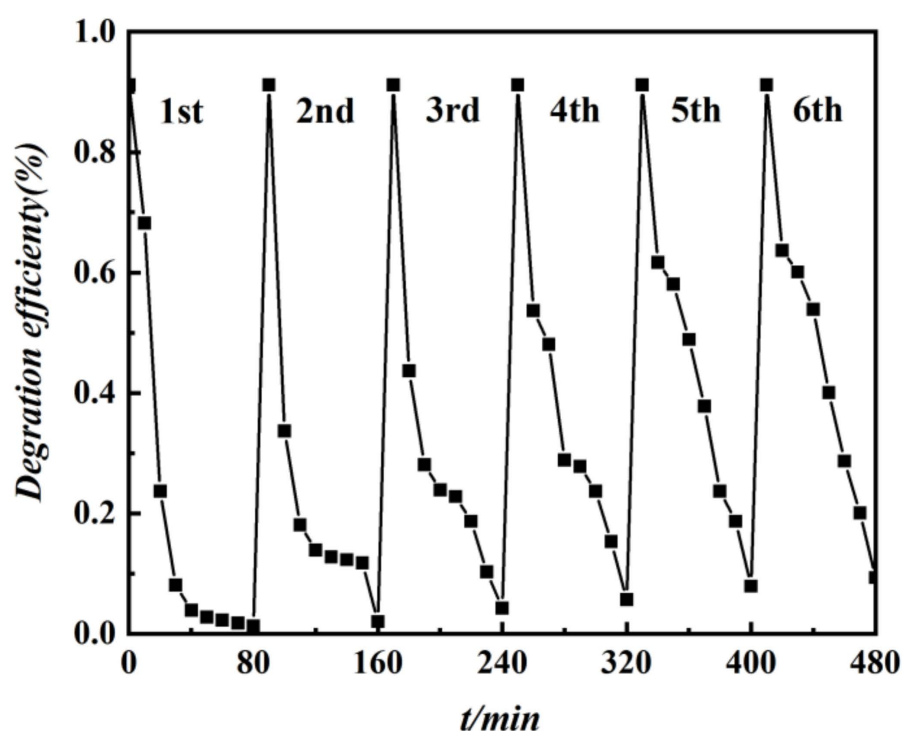


Figure 12. Regeneration and reusability of the photocatalyst in different cycles.

3.5. X-Ray Photoelectron Spectroscopy (XPS) Analysis of Reused Samples

To confirm the expected compositions of the last reused Zn-ZSM-5 samples, compared with pure ZSM-5, all peaks (O 1s, Zn 2p, Al 2p, Si 2s and Si 2p) relevant to this study are identified, as shown in Figure 13a and Table 2. The full-range X-ray photoelectron spectroscopy (XPS) spectra results seen in Figure 1 qualitatively revealed the existence of Si 2s, Si 2p, Al 2p and O 1s in pure ZSM-5, with atomic percent accounts for 9.45%, 11.69%, 1.15% and 40.50%, respectively. High-resolution XPS spectra of Zn-ZSM-5 samples (n(Zn)/n(Si) of 1:100), which reveals not only the existence of Si 2s, Si 2p, Al 2p and O 1s, with atomic percent accounts for 9.65%, 12.23%, 1.16% and 42.88%, but also the existence of Zn 2p, with atomic percent accounts for 0.61%. Thus, it can be concluded that the partial metal cations of Zn is located in the framework of Zn-ZSM-5 samples. Figure 13b shows that the peak of Zn 2p XPS spectra in Zn-ZSM-5 samples appears three bonding environments, which are Zn-OH⁺ (1023.5 eV), ZnO (1021.7 eV), Zn 2p 3/2 (1021.4 eV) [30]. Among of them, the higher binding energy of zinc species (1023.5 eV) is mainly due to the formation of Zn-OH⁺ with the framework of ZSM-5 zeolite, the binding energy of zinc species between 1021.7 eV and 1021.4 eV comes from the sub-nano-sized ZnO particles with small size moieties in micro-mesoporous zeolite [19].

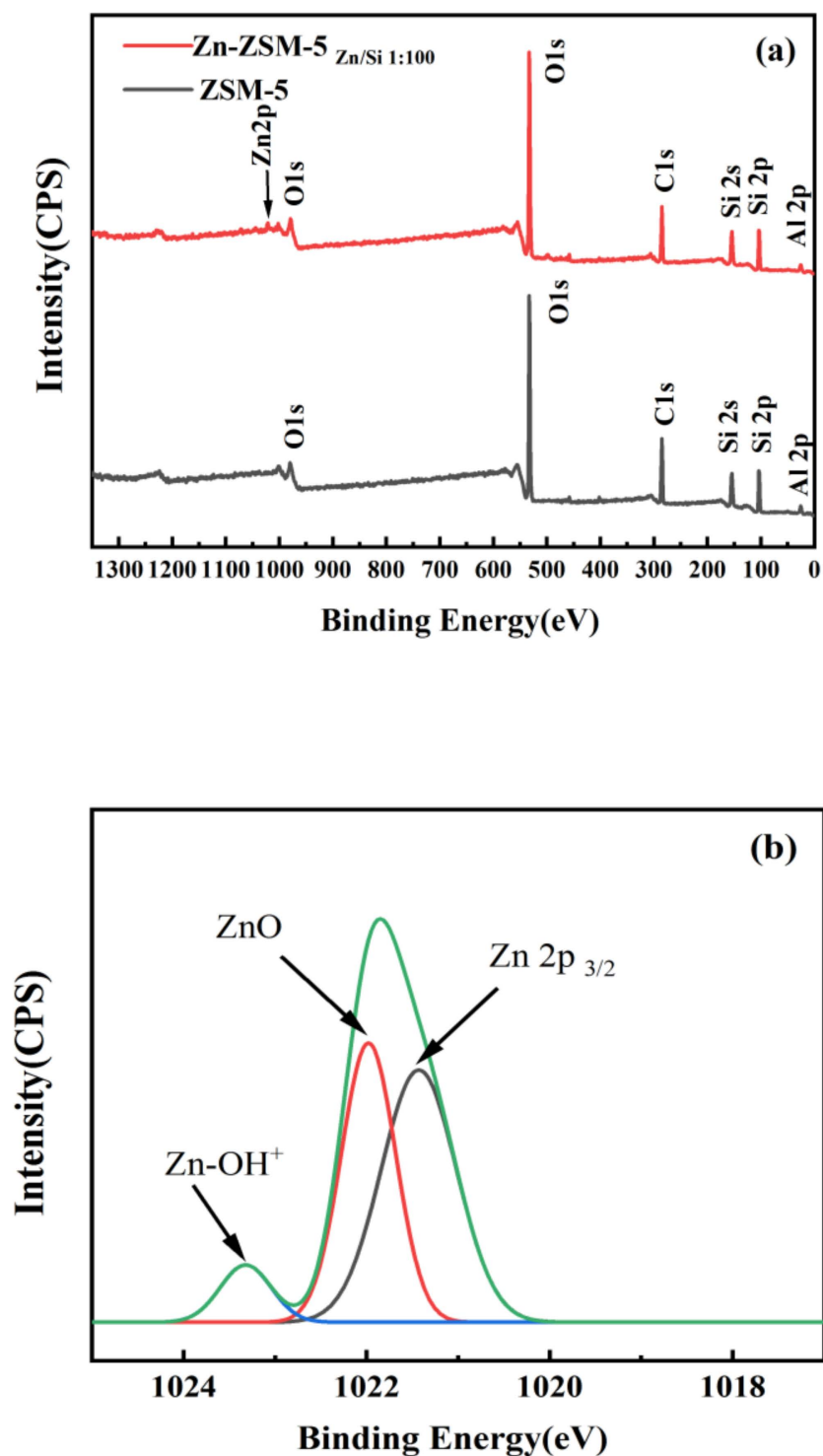


Figure 13. X-ray photoelectron spectroscopy (XPS) survey spectra of (a) pure ZSM-5 and Zn-ZSM-5 (Zn/Si = 1:100) and (b) Zn 2p in Zn-ZSM-5 composite products (n(Zn)/n(Si) of 1:100).

Table 2. Atomic percent accounts of pure ZSM-5 and Zn-ZSM-5 from XPS survey spectra (Unit: %).

Sample	O1s	Zn2p	C1s	Si2s	Si2p	Al2p
ZSM-5	40.5	0.00	37.20	9.45	11.69	1.15
Zn-ZSM-5	42.88	0.61	33.46	9.65	12.23	1.16

4. Experimental

4.1. Synthesis of Hierarchical Zn-ZSM-5 Composite Photocatalysts

Alkali-modified attapulgite [31] and 9% (mass fraction) hydrochloric acid were transferred into a hydrothermal crystallization kettle in the solid-liquid ratio of 1:8, followed by hydration at 180 °C for 12 h. The solution was centrifuged, rinsed and dried to obtain a zeolite precursor Si-ATP.

Accurately weighed amounts of 0.055 g NaAlO_2 , 0.118 g polyethylene oxide–polypropylene oxide–polyethylene (PEO-PPO-PEO, short for P123) as mesoporous template, 0.55 g tetrapropylammonium bromide (TPABr) microporous template and various amounts of $\text{Zn}(\text{NO}_3)_2$ were mixed and dissolved in 5.20 mL of deionized water. Next, 0.8 g Si-ATP and 2.1 mL NaOH solution (1 mol/L) were added and stirred in a water bath at 60 °C for 2 h to obtain the initial gel. Next, the samples were transferred to a hydrothermal PTFE crystallization reactor, which was sealed and crystallization was carried out at 180 °C for 36 h in a conventional oven (DZF-603, Shanghai Jinghong Experimental Equipment Co., Ltd.). After carrying out the reaction process, the reaction was allowed to cool down naturally to room. All of the synthesized products were washed by centrifuging repeatedly with distilled deionized water, and subsequently dried at 80 °C for 6 h in ambient condition, then calcination in a muffle furnace at 550 °C for 5 h to remove the template agent, leading to the final product. The amount of $\text{Zn}(\text{NO}_3)_2$ was adjusted to 5 different values of 0, 1.98, 3.96, 7.92 and 15.84 mg to obtain pure ZSM-5 zeolite and Zn-ZSM-5 composites with Zn/Si ratios of 1:200, 1:100, 1:50 and 1:25, respectively. The samples were named as sample a, b, c, d and e, respectively.

4.2. Sample Characterization

An X-ray diffractometer (Shimadzu, Tokyo, Japan) was used to analyze the crystallography of the synthesized samples. The morphology was tested by SEM using an FEI Quanta-450-FEG (FEI Company, Hillsboro, OR, USA). The light response of the samples was evaluated by an Evolution 220 dual-beam UV–Vis spectrophotometer (Thermo Fisher Scientific Company, Waltham, MA, USA). The N_2 adsorption-desorption isotherms of the samples were measured using a Micromeritics ASAP 2020 PlusHD88 (New York, NY, USA) equipment. The total pore volume was obtained by converting the nitrogen adsorption capacity into the volume of liquid nitrogen at the relative pressure (P/P_0) of 0.95.

4.3. Photocatalytic Degradation Evaluation

Tests of the photocatalytic activity of the synthesized Zn-ZSM-5 zeolite photocatalyst were carried out under UV radiation. First, 50.00 mg of methylene blue dye as the target pollutant were dissolved in 1.00 L deionized (DI) water and heated to 60 °C for 8 h to simulate dyeing wastewater. For each degradation solution, 20 mg of sample and 0.1 mL of 30% (mass fraction) H_2O_2 solution were added into 100 mL of the methylene blue solution, and the mix was transferred to the photocatalytic reactor. Under dark conditions, the adsorption equilibrium was achieved by magnetic stirring for 60 min. After turning on a 500 W mercury light source, 5 mL of degradation solution was taken out every 10 min. The solution was firstly filtered through a microporous membrane ($d = 0.45 \mu\text{m}$) and the absorbance of the solution at the methylene blue (MB) maximum absorption wavelength of $\lambda = 664 \text{ nm}$ was measured by an UV–visible spectrophotometer (UV757CRT, Shanghai Precision Scientific Instrument Co., Ltd. China).

4.4. Repeatability Experiment of Photocatalytic Degradation

Collecting and setting the suspension of photocatalyst particles until 48 h, then the filtrate was filtered to colorless. The acquired photocatalytic material is put into muffle furnace calcined for 4 h. The obtained samples were subjected to photocatalytic tests according to the previous test conditions.

5. Conclusions

By varying the amount of $\text{Zn}(\text{NO}_3)_2$ precursor, Zn-ZSM-5 zeolite photocatalysts with different Zn/Si ratio were synthesized by a one-step hydrothermal synthesis method. It was shown that the Zn/Si ratio has a significant impact on the crystal structure, surface morphology, photo-response activity and texture characteristics. The Zn/Si ratio exhibits an optimal value of 1:100, where the basic framework and the Zn-ZSM-5 composite display an MFI-type topology. The pore structure was found to be rather regular with a uniform pore size distribution.

The $\text{Zn}(\text{NO}_3)_2$ precursor is transformed into sub-nanometer ZnO clusters during synthesis, where the clusters are assembled on the surface and inside of the hierarchical ZSM-5 zeolite. The synthesized Zn-ZSM-5 zeolite then contains more photocatalytic active site, which improves the enrichment efficiency of MB, facilitates the photocatalytic reactions, which leads to a synergistic effect of enhanced adsorption on the composite surface and improved photocatalytic activity. However, excessive addition of zinc leads to a blocking of the pores and the zeolite framework structure collapses, resulting in an insignificant photocatalytic degradation rate.

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