

## Research Article

# Characteristics and Performance of Nanozinc Oxide/Mesoporous Silica Gel Photocatalytic Composite Prepared by a Sol-Gel Method

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Nano-ZnO loaded mesoporous SiO<sub>2</sub> was prepared by sol-gel technology as a photocatalytic composite. XRD, SEM, TEM, EDX, and N<sub>2</sub> sorption isotherms were used to characterize the nano-ZnO/mesoporous SiO<sub>2</sub>. Acid Red 18 was used as simulated pollutant to determine the photocatalytic performance of nano-ZnO/mesoporous SiO<sub>2</sub> under ultraviolet light and solar light. The results showed that 6.4 nm ZnO was obtained and immobilized on mesoporous SiO<sub>2</sub>. Compared to the mesoporous SiO<sub>2</sub>, the surface area and average pore width of nano-ZnO/mesoporous SiO<sub>2</sub> were reduced by 12 m<sup>2</sup>/g and 0.7 nm, respectively. 50% ZnO content in a composite calcinated at 200°C exhibited the best photocatalytic activity. The removal of Acid Red 18 under solar irradiation was 10% higher than ultraviolet light.

## 1. Introduction

Zinc oxide (ZnO) is an important *n*-type semiconductor with a wide-bandgap energy of 3.37 eV [1] and an exciton binding energy of 60 meV at room temperature. ZnO is suitable as a photocatalyst for decomposing organic contamination in aqueous solutions and can present a higher photocatalytic activity than TiO<sub>2</sub> [2, 3]. Compared with bulk ZnO, nanopowder ZnO improves the catalytic activity due to the quantum size effect [4]. Su et al. prepared quantum-sized ZnO for photocatalytic degradation of the reactive dye “brilliant blue X-BR” with nearly 100% color removal [5]. In a subsequent study, nano-ZnO under UV irradiation exhibited about 100% removal of “Acid Yellow 23” within 60 min [6].

However, nano-ZnO is so small that it is difficult to recycle from aqueous solutions following photocatalytic processes, which limits its application in water treatment. To overcome this shortcoming, Motshekga et al. developed a composite photocatalyst on which nano-ZnO was immobilized on larger particle carriers [7]. Mesoporous SiO<sub>2</sub> is an excellent carrier for catalysis [8, 9] because it provides an increased catalytic space over microporous carriers, which is advantageous for adsorption of molecular dye. Mesoporous

SiO<sub>2</sub> could decrease the dosage of the nano-ZnO and increase the utilization rate. On the other hand, mesoporous SiO<sub>2</sub> could improve the dispersion of nano-ZnO and reduce the reunion.

In this study, a photocatalytic composite of nano-ZnO immobilized on mesoporous SiO<sub>2</sub> was prepared by a sol-gel method. X-ray diffraction, N<sub>2</sub> sorption isotherms, scanning electron microscopy, transmission electron microscopy, and energy-dispersive spectroscopy were used to comprehensively characterize the nano-ZnO/mesoporous SiO<sub>2</sub> composite. Acid Red 18 was used as a simulated pollutant to determine the photocatalytic performance of our composite under ultraviolet or solar light.

## 2. Experimental

**2.1. Preparation of Nano-ZnO/Mesoporous SiO<sub>2</sub> Composite.** To prepare the nano-ZnO/mesoporous SiO<sub>2</sub> composite, 1.10 g zinc acetate was dissolved with stirring in 50 mL anhydrous ethanol at 80°C. A certain quantity of mesoporous silica gel was added to the zinc acetate solution to form a hybrid system. A lithium hydroxide solution of 0.29 g lithium hydroxide and 50 mL anhydrous ethanol was added with 100 mL

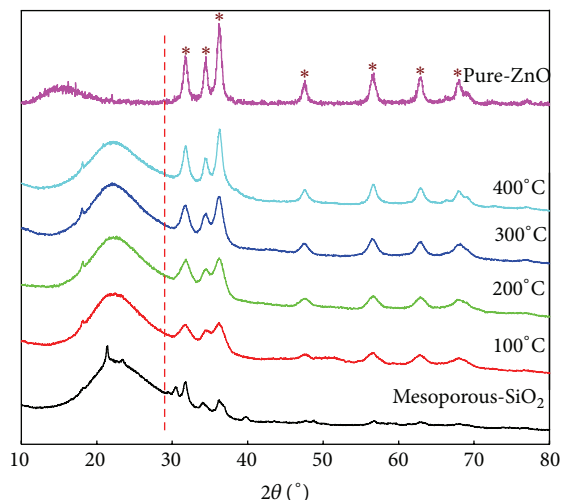


FIGURE 1: XRD of ZnO, SiO<sub>2</sub>, and ZnO/SiO<sub>2</sub> from different calcination temperatures.

*n*-hexane at room temperature to the hybrid system. A white gel was obtained by overnight refrigeration, from which a solid was obtained by centrifugation and drying at 100°C. The nano-ZnO/mesoporous SiO<sub>2</sub> composite was prepared by calcination at 200 to 400°C over 2 h.

**2.2. Characterization of Materials.** The crystal phases of nano-ZnO/mesoporous SiO<sub>2</sub> were analyzed by X-ray diffraction (XRD) on a PaNalytical X-ray diffractometer (X'Pert Pro MPD, Netherlands) using Cu K $\alpha$  radiation. Scanning electron microscopy (SEM) was performed by a Nova NanoSEM (FEI, USA) with energy-dispersive X-ray spectroscopy (EDX). Transmission electron microscope (TEM) was carried out using a JEM-2010 (JEOL, Japan). N<sub>2</sub> sorption isotherms were measured using a Micromeritics ASAP2020 system (USA).

**2.3. Photocatalytic Experiment.** Acid Red 18 was used to determine photocatalytic performance. The maximum absorption wavelength of Acid Red 18 was 506 nm. To assess photocatalytic activity, 200 mL of 20 mg/L Acid Red 18 and a certain dosage of nano-ZnO/mesoporous SiO<sub>2</sub> were added to a 250 mL beaker with magnetic stirring. A 10 cm long mercury UV lamp (10 W Guangdong Bright Star) was used as the radiation source with a wavelength of 245 nm. The solar light experiment was carried out under sunlight irradiation. After a certain reaction interval of 40 min, a 10 mL sample was removed and centrifuged at 12000 rpm to remove the catalyst. The dyestuff absorbance of Acid Red 18 was analyzed by a UV-2102PC UV-Vis spectrophotometer (UNICO, China) after centrifuging. The degradation rate of Acid Red 18 was calculated by the following equation:

$$\text{Removal} = \frac{(C_0 - C_t)}{C_0} \times 100\%. \quad (1)$$

Here,  $C_0$  was the initial concentration of Acid Red 18 and  $C_t$  was the concentration of Acid Red 18 at  $t$  time.

### 3. Results and Discussion

**3.1. XRD Analysis.** Figure 1 shows XRD analysis of ZnO, mesoporous SiO<sub>2</sub>, and nano-ZnO/mesoporous SiO<sub>2</sub> composites at different calcination temperature from 100°C to 400°C. XRD of mesoporous SiO<sub>2</sub> yields an intense peak from 20 to 30° [10]. The large band (not a peak) between 20° and 30° is easily ascribed to amorphous silica. The ZnO characteristic peaks are shown at  $2\theta$  values of 31.7, 34.4, 36.2, 47.5, 56.5, 62.8, 67.9, and 68.8° in Figure 1. All peaks can be well indexed to standard patterns (JCPDS 36-1451) without any impurity phases [11]. The major peaks of ZnO at  $2\theta$  values of 31.7, 34.4, 36.2, and 47.5° can be indexed to (100), (002), (101), and (102) crystal planes and characteristic ZnO peaks become obvious at calcination temperatures above 200°C. From Figure 1, it can be seen clearly that the half peak widths of characteristic peaks gradually reduce with increasing calcination temperatures. This indicates that ZnO particle sizes increase with calcination temperature. According to the Scherrer equation [12], the ZnO particle size of composite was 6.4 nm. Furthermore, the crystalline peaks suggest that the sample measured is already zinc precursor impregnated silica and not pure silica.

**3.2. N<sub>2</sub> Sorption Analysis.** Figure 2 shows that both nano-ZnO/mesoporous SiO<sub>2</sub> and mesoporous SiO<sub>2</sub> exhibit type IV isotherms [13] with high surface areas (318 and 330 m<sup>2</sup>/g) and average pore widths (7.9 and 8.6 nm), respectively. Thus, compared with mesoporous SiO<sub>2</sub>, the surface area and average pore width of the composite fell by 12 m<sup>2</sup>/g and 0.7 nm, respectively. This suggests that nano-ZnO is confined inside the pores of mesoporous SiO<sub>2</sub>.

**3.3. Morphological Analysis.** The SEM of nano-ZnO/mesoporous SiO<sub>2</sub> (Figure 3(a)) shows a large particle size, which is advantageous for catalyst recovery from aqueous solutions. From the EDX analysis of the composite, the atomic ratio of Zn to Si is about 3:4. Thus, the mass content of ZnO

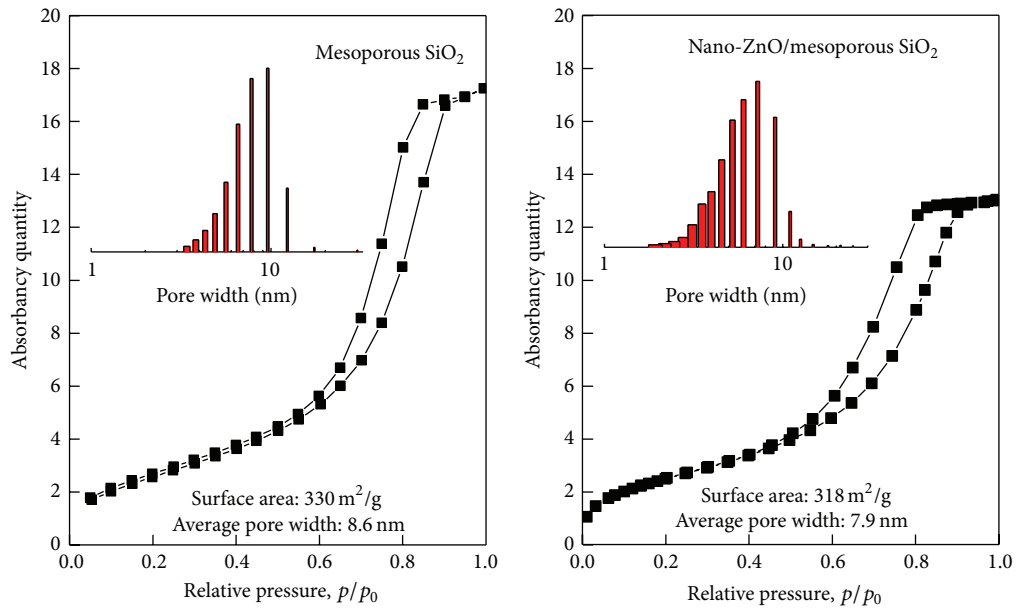


FIGURE 2: Comparison of nitrogen isotherm data showing pore size distribution for SiO<sub>2</sub> and ZnO/SiO<sub>2</sub>.

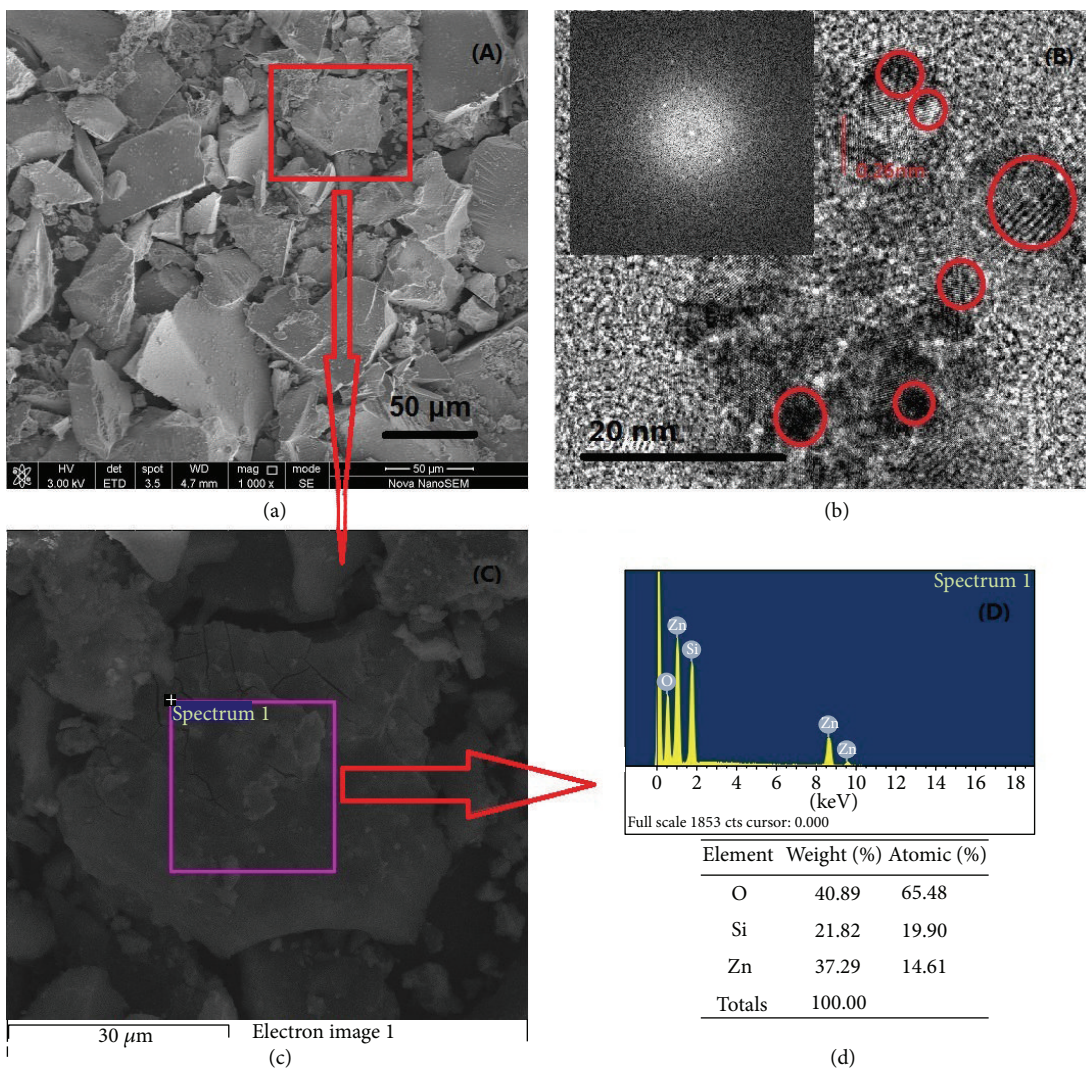


FIGURE 3: SEM, TEM, and EDX of nano-ZnO/mesoporous SiO<sub>2</sub> (50% ZnO).

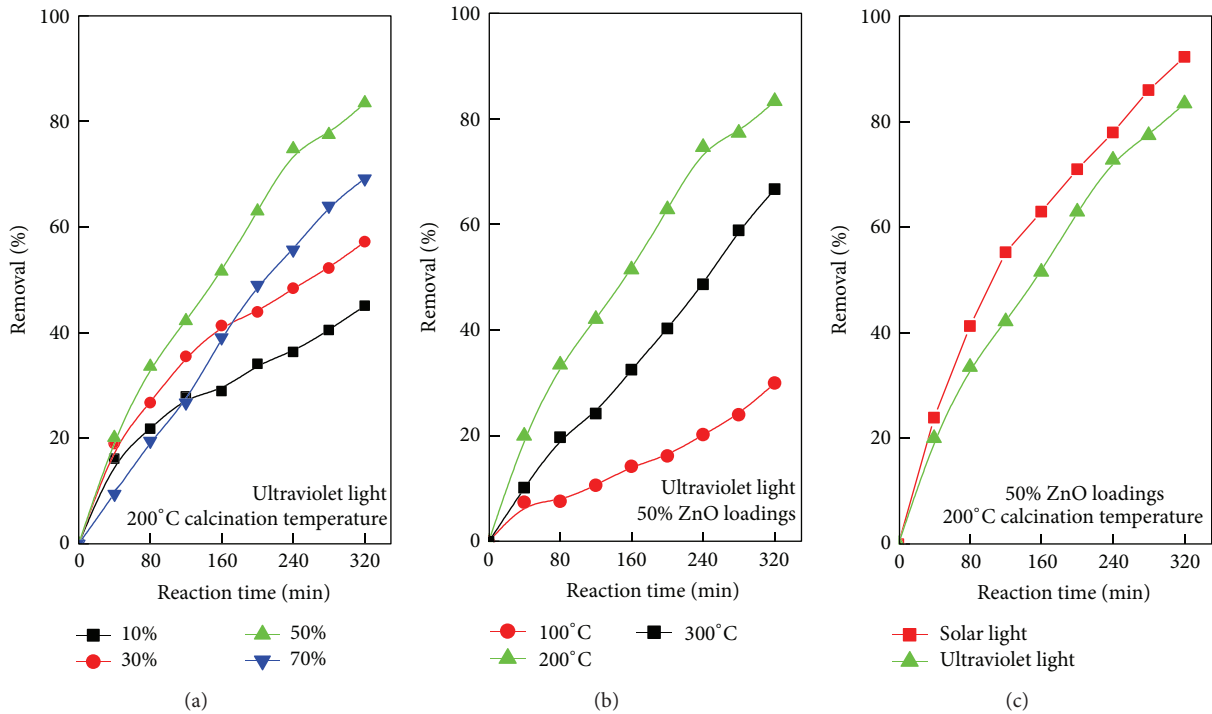


FIGURE 4: Photocatalytic performance of nano-ZnO/mesoporous SiO<sub>2</sub> ((a) ZnO loadings effect; (b) calcination temperature effect; (c) light source effect).

in the composite is about 57%, close to the theoretical 50% ZnO content. From TEM of the composite (Figure 3(b)), the ZnO particle sizes are shown to be on the nanoscale, which is similar to the results of the XRD analysis. Combined with SAED, the TEM image shows sharp lattice fringes with 0.26 nm spacing in the nano-ZnO/mesoporous SiO<sub>2</sub>, corresponding to the (002) planes of wurtzite phase ZnO crystals.

**3.4. Photocatalytic Activity Test of Composite.** Figure 4(a) shows the photocatalytic performance of nano-ZnO/mesoporous SiO<sub>2</sub> composites with various ZnO contents from 10% to 70%. The composite with 50% ZnO content showed the best photocatalytic activity with 83.5% removal of Acid Red 18 at 320 min. Excessive ZnO in the composite may cause aggregation to yield increased particle sizes, which can reduce the quantum size effect. Mesoporous SiO<sub>2</sub> has a great adsorption amount of Acid Red 18. The high ZnO content means the low SiO<sub>2</sub> in composite photocatalyst.

The decline of adsorption ability is also causing the decrease of catalytic activity. Under UV irradiation, electronic (e<sup>-</sup>) can be agitated from valence band (VB) to conduction band (CB) of ZnO to produce hole (h<sup>+</sup>). The hole can react with hydroxyl ion to generate hydroxyl radical (•OH). The •OH shows a strong oxidation ability to decompose the organic contamination in aqueous. The number of •OH can be increased with the rise of nano-ZnO content in nano-ZnO/mesoporous SiO<sub>2</sub>. However, excessive ZnO in composite photocatalyst may aggregate together to increase nano-ZnO particle size. The big particle size of ZnO can reduce the quantum size effect and decrease the catalytic activity.

On the other hand, mesoporous SiO<sub>2</sub> has a good ability of adsorption of organic contaminants. The high ZnO content means the low mesoporous SiO<sub>2</sub> in composite photocatalyst. The decline of adsorption ability of ZnO/mesoporous SiO<sub>2</sub> is also causing the decrease of catalytic activity. So, the 50% ZnO content in ZnO/mesoporous SiO<sub>2</sub> composite is optimal value in this study.

The precursor obtained after sol-gel procedure was treated by calcination. The nano-ZnO/mesoporous SiO<sub>2</sub> composites were prepared at different calcination temperatures at 100°C, 200°C, and 300°C. The catalytic activity of nano-ZnO/mesoporous SiO<sub>2</sub> composite is shown in Figure 4(b). From Figure 4(b), it is shown clearly that the high photocatalytic activity of nano-ZnO/mesoporous SiO<sub>2</sub> composites is calcinated at 200°C. Higher calcination temperature can cause particle aggregation and result in a decrease in photocatalytic activity.

Finally Figure 4(c) shows that the degradation of Acid Red 18 under solar irradiation was 10% higher than under ultraviolet irradiation. This is because sunlight contains a mixed spectrum and nano-ZnO/mesoporous SiO<sub>2</sub> composites can use wider ranges of light, leading to 93% degradation under solar light irradiation.

## 4. Conclusions

A photocatalytic composite of nano-ZnO immobilized on mesoporous SiO<sub>2</sub> was prepared using a sol-gel process. 6.4 nm ZnO was obtained and immobilized on mesoporous SiO<sub>2</sub>. Compared to mesoporous SiO<sub>2</sub>, the surface area and average pore width of nano-ZnO/mesoporous SiO<sub>2</sub>

decreased by  $12 \text{ m}^2/\text{g}$  and  $0.7 \text{ nm}$ , respectively. Composites with a ZnO composition of 50% prepared at  $200^\circ\text{C}$  calcination temperature had the best photocatalytic activity, achieving 95% color removal at 320 min under solar light. The removal of Acid Red 18 under solar irradiation was 10% higher than under ultraviolet light.

## Conflict of Interests

The authors declare that they have no conflict of interests.

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## References

- [1] K. Sowri Babu, A. Ramachandra Reddy, C. Sujatha, and K. Venugopal Reddy, "Effects of precursor, temperature, surface area and excitation wavelength on photoluminescence of ZnO/mesoporous silica nanocomposite," *Ceramics International*, vol. 39, no. 3, pp. 3055–3064, 2013.
- [2] M. A. Behnajady, N. Modirshahla, and R. Hamzavi, "Kinetic study on photocatalytic degradation of C.I. Acid Yellow 23 by ZnO photocatalyst," *Journal of Hazardous Materials*, vol. 133, no. 1-3, pp. 226–232, 2006.
- [3] I. Fatimah, S. Wang, and D. Wulandari, "ZnO/montmorillonite for photocatalytic and photochemical degradation of methylene blue," *Applied Clay Science*, vol. 53, no. 4, pp. 553–560, 2011.
- [4] R. Hong, T. Pan, J. Qian, and H. Li, "Synthesis and surface modification of ZnO nanoparticles," *Chemical Engineering Journal*, vol. 119, no. 2-3, pp. 71–81, 2006.
- [5] S. Su, S. X. Lu, and W. G. Xu, "Photocatalytic degradation of reactive brilliant blue X-BR in aqueous solution using quantum-sized ZnO," *Materials Research Bulletin*, vol. 43, no. 8-9, pp. 2172–2178, 2008.
- [6] N. Modirshahla, A. Hassani, M. A. Behnajady, and R. Rahbarfam, "Effect of operational parameters on decolorization of Acid Yellow 23 from wastewater by UV irradiation using ZnO and ZnO/SnO<sub>2</sub> photocatalysts," *Desalination*, vol. 271, no. 1-3, pp. 187–192, 2011.
- [7] S. C. Motshekga, S. S. Ray, M. S. Onyango, and M. N. B. Momba, "Microwave-assisted synthesis, characterization and antibacterial activity of Ag/ZnO nanoparticles supported bentonite clay," *Journal of Hazardous Materials*, vol. 262, no. 5, pp. 439–446, 2013.
- [8] C. Cannas, M. Mainas, A. Musinu, and G. Piccaluga, "ZnO/SiO<sub>2</sub> nanocomposites obtained by impregnation of mesoporous silica," *Composites Science and Technology*, vol. 63, no. 8, pp. 1187–1191, 2003.
- [9] L.-Y. Lin and H. Bai, "Salt-templated synthesis of Ce/Al catalysts supported on mesoporous silica for acetone oxidation," *Applied Catalysis B: Environmental*, vol. 148-149, pp. 366–376, 2014.
- [10] B. Jeong, D. H. Kim, E. J. Park et al., "ZnO shell on mesoporous silica by atomic layer deposition: removal of organic dye in water by an adsorbent and its photocatalytic regeneration," *Applied Surface Science*, vol. 307, pp. 468–474, 2014.
- [11] H. Xu, T. L. Yu, and J. F. Liu, "Photo-degradation of Acid Yellow 11 in aqueous on nano-ZnO/Bentonite under ultraviolet and visible light irradiation," *Materials Letters*, vol. 117, no. 3, pp. 263–265, 2014.
- [12] W. G. Xu, S. F. Liu, S. X. Lu, S. Y. Kang, Y. Zhou, and H. F. Zhang, "Photocatalytic degradation in aqueous solution using quantum-sized ZnO particles supported on sepiolite," *Journal of Colloid and Interface Science*, vol. 351, no. 1, pp. 210–216, 2010.
- [13] Q. Tang, H. Xu, Y. Y. Zheng, J. F. Wang, H. S. Li, and J. Zhang, "Catalytic dehydration of methanol to dimethyl ether over micro-mesoporous ZSM-5/MCM-41 composite molecular sieves," *Applied Catalysis A: General*, vol. 413-414, no. 1, pp. 36–42, 2012.



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