

Photocatalytic activity of ZnO /HZSM-5 in degradation of 4-nitrophenol in aqueous solution

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Abstract

Nanometric ZnO clusters confined in HZSM-5 were prepared with different ZnO loadings and characterized by X-ray diffraction (XRD) and TEM. The photocatalytic degradation of 4-nitrophenol in aqueous solution was carried out by using supported ZnO on HZSM-5 under UV light. The influence of various parameter such as ZnO loading amounts in catalyst and pH on degradation was optimized. The experimental results demonstrated that the presence of zeolite in ZnO/HZSM-5 catalysts could enhance adsorption as well as degradation of 4-nitrophenol. It is suggested that encapsulating the semiconductor cluster in the porous support is a possible way to inhibit or to retard the electron-hole recombination. The higher activity of ZnO /HZSM-5 is mainly due to fine dispersion of ZnO and hydrophobicity of support.

Keywords: ZnO, HZM-5, 4-nitrophenol.

1-Introduction

Zinc Oxide (ZnO) an important semiconductor material with a band gap of 3.37 eV and exciton Bohr radius of 1.8 nm, has attracted much attention due to its promising applications in commercial devices such as a solar cell, photocatalysis, light emission, gas sensor, and other optical devices [1,3]. As we know, when the particle sizes of many semiconductors, ZnO included, decrease to exciton Bohr radius scales, these materials usually exhibit quantum size effects, presenting different electric and optical properties from bulk materials.

The study on subnanometric ZnO clusters as a medium between single molecules and nanocrystals is an active area now days, Since ZnO clusters are so small and unstable, many materials, such as glass, polymers and zeolites, are used as supports or stabilizers in the various

preparation methods. Using microporous zeolites as host, they provide well-defined and well-ordered pores to confine the ZnO clusters [2, 3].

Nitrophenols are some of the most refractory pollutants, which can be present in industrial wastewater. In particular, 4-nitrophenol and its derivatives result from the production processes of pesticides, herbicides and synthetic dyes. These pollutants have high toxicity and carcinogenic character [4]. ZnO has been reported sometimes to be more efficient than TiO₂ for the photo oxidation of phenol and nitrophenol [5, 6].

In this work, different amounts of ZnO clusters were prepared in the pores of HZSM-5 (MFI type) microporous zeolites by the incipient impregnation method. Photocatalytic efficiency of ZnO/HZSM-5 samples with different ZnO loading amounts was investigated under advanced oxidation process.

2. Experimental

a. Sample Preparation. HZSM-5 was obtained by calcining NH₄ZSM-5 at 500 °C for 5 h. A special volume of Zn(acac)₂ ethanol solution was added into 1.00 g of zeolite powder with continuous stirring for 2h, and then it was stirred under a hot water bath until dried. After this powder was kept at 120 °C overnight, it was calcined at 500 °C for 5 h. To achieve different ZnO loadings materials, the concentration of Zn(acac)₂ ethanol solutions was adjusted.

b. Photocatalytic Experiments. A batch photoreactor of cylindrical shape containing 100 ml of aqueous suspension was used. A 30 W medium-pressure Hg lamp was used for irradiation in all experiments. The amount of catalyst used for all of the experiments was 0.5 g and the initial 4-nitrophenol concentration was 20 mg L⁻¹. The initial pH of the suspension was adjusted to 5 by addition of H₂SO₄. The photoreactivity runs lasted 90min including the first 15 minute during which the lamp was switched off. Samples of 5 ml volume were withdrawn from the suspensions every 15 or 25 min and the catalysts were separated from the solution by centrifuging. The

quantitative determination of 4-nitrophenol was performed by measuring its absorption at 315 nm. Finally, total organic carbon (TOC) determinations were carried out for all of the runs.

c. Instrumental Measurements.

The powder X-ray diffraction (XRD) patterns were recorded on Siemens diffractometer with Cu K α radiation source. Transmission electron microscope (TEM) measurements were taken on a Philips CM 200 FEG (Field Emission Gun). UV-Vis absorption of 4-nitrophenol with a Shimadzo 1700 spectrophotometer. TOC analysis performed by Skalar formacs.

3-Results and Discussion

3-1-catalyst structure

Figure1 shows the XRD patterns of ZnO/HZSM-5 with different ZnO loadings. In the XRD patterns of ZnO/HZSM-5 with different ZnO loadings all these materials maintain good zeolite crystal structure. At low ZnO loading, no diffraction peak of macrocrystalline ZnO exists. At high ZnO loading, the diffraction peaks of ZnO with wurtzite structure appear and develop with increasing loading. The invisibility of the ZnO diffraction peaks indicates that ZnO has been highly dispersed on the surface of the support.

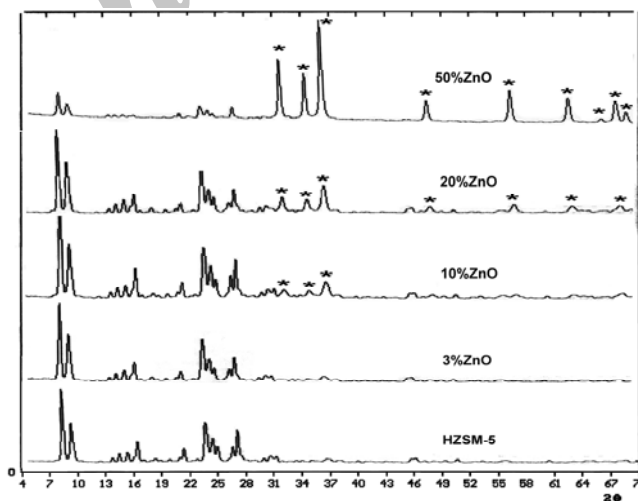


Figure1. XRD patterns of ZnO/HZSM-5 with different ZnO loadings

Further morphology and structural investigations of ZnO supported on HZSM-5 were performed using TEM.

Figure 2 shows the TEM image of ZnO/HZSM-5 with 20.0 wt % ZnO loading. In figure 2 (a) clearly observed that ZnO particles covered the extra surface of HZSM-5. This image indicates that nanoparticles are

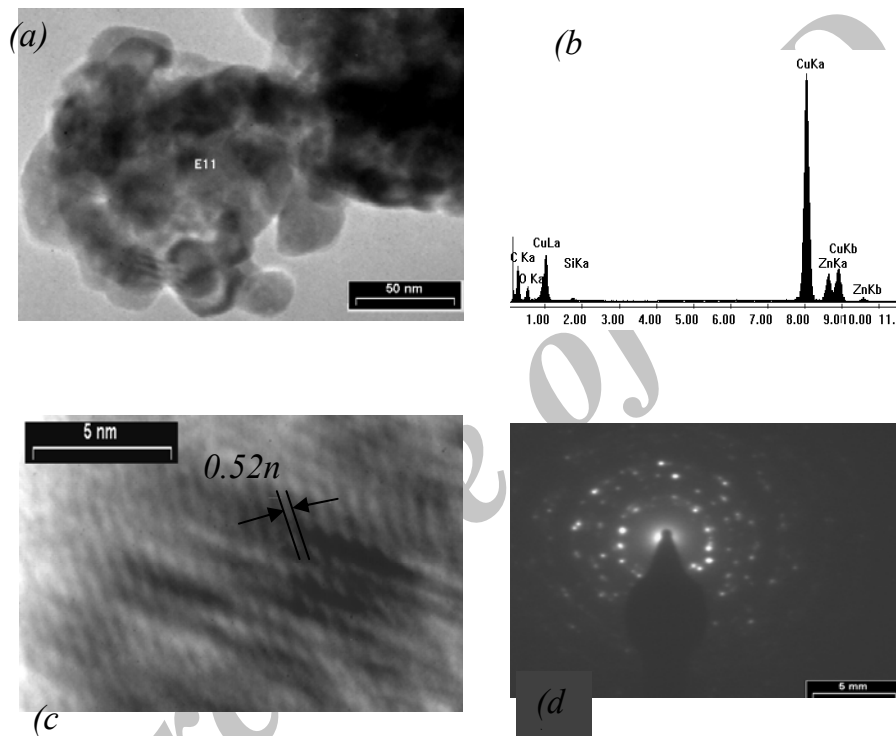


Figure 2. (a) TEM image of ZnO/HZSM-5 with 20.0 wt % ZnO loading, (b) EDX diagram of ZnO/HZSM-5, (c) HRTEM image of ZnO/HZSM-5 nanoparticle, (d) SAED pattern of ZnO nanoparticle.

of monodisperse nearly spherical shape with an average particle size 15-25 nm. The corresponding high-resolution TEM Fig. 2(c) confirms that the nanoparticles are polycrystalline and the lattice spacing of 0.52 nm agree with the ZnO Wurtzite hexagonal structure, which is also supported by SAED (Selected Area Electron Diffraction).

3-2-photocatalytic activity

Photocatalytic efficiency of ZnO/HZSM-5 samples with different ZnO loading amounts in Photodegradation and mineralization of 4-nitrophenol was checked by UV-Vis absorption of 4-nitrophenol and also by determining the total organic carbon (TOC) at 25 min intervals.

Effect of ZnO loading amounts

Figure3 shows the effect of different ZnO loading amounts on the percentage of Photodegradation of 4-nitrophenol followed by UV-Vis absorption of 4-nitrophenol at 315 nm wavelength. Although all catalysts had good performance, ZnO/HZSM-5 (7%) showed highest activity. The fine dispersion of ZnO and hydrophobicity of the support are the major factors for the high degradation.

Prior to photocatalytic process, the large amount of 4-NPh adsorbed (dark) over HZSM-5 is due to hydrophobicity of HZSM-5. Furthermore, the presence of acid sites in HZSM-5 could also be the reason for better adsorption of 4-NPh [8].

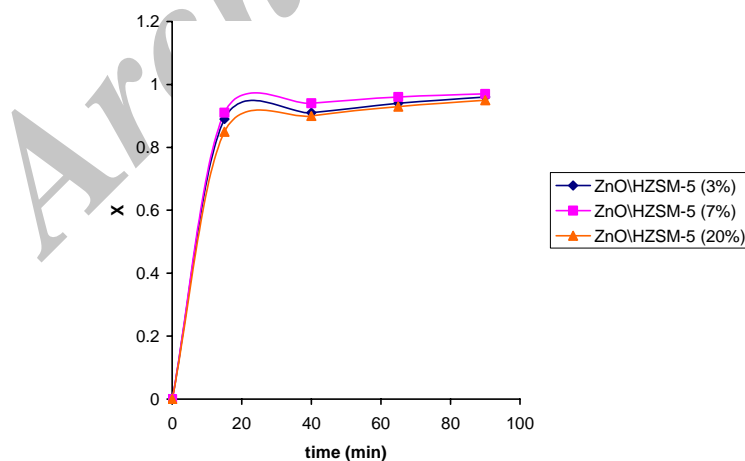


Figure3. Effect different of ZnO loading amounts on the percentage of Photodegradation of 4-nitrophenol

In figure 4 TOC concentrations versus irradiation time is reported. TOC concentration decrease after 15 min in dark which is related to high adsorption of 4-NPh on HZSM-5. An increasing in TOC concentration is observed after 40min because of turning some adsorbed organic molecules into solution after that because of photo degradation, TOC concentration decrease gradually.

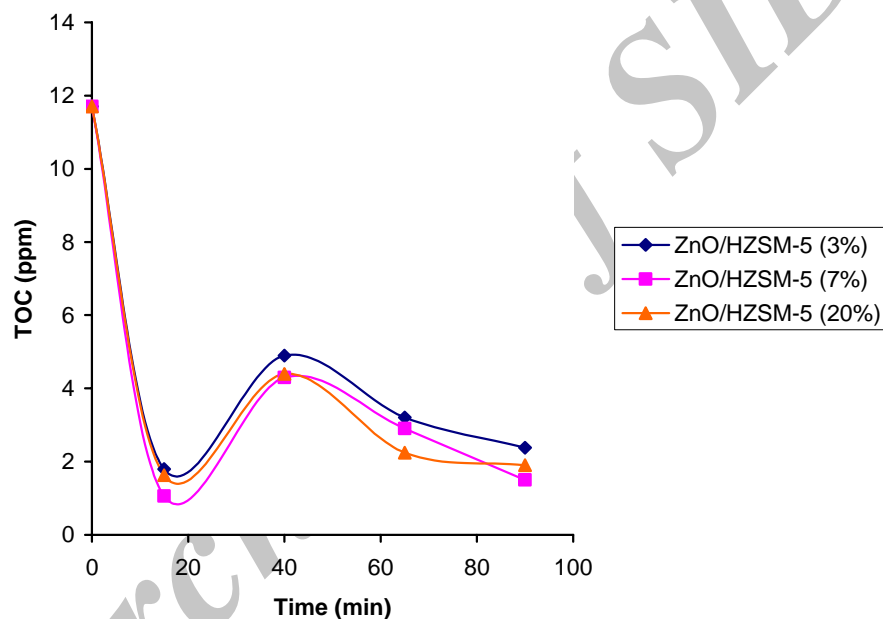


Figure4. TOC concentration versus irradiation time

Effect of solution pH

The pH of the solution determines the surface charge properties of the photocatalyst and therefore the adsorption behavior towards the pollutants. Figure 5 shows the degradation of 4-nitrophenol on ZnO/HZSM-5 with 7% loading amount at different pH.

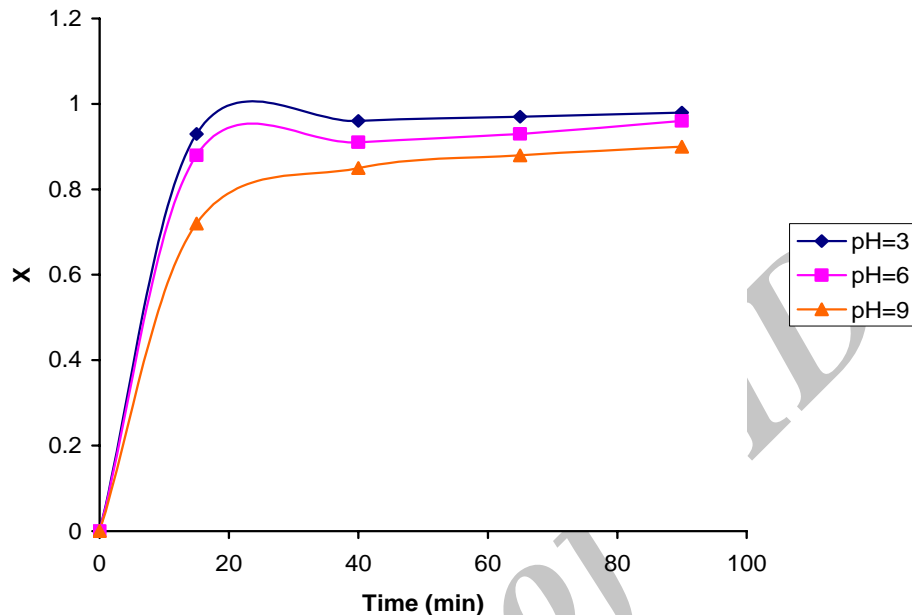


Figure5. Degradation of 4-nitrophenol on ZnO/HZSM-5 7% loading amount at different pH

It can be concluded these reactions were favored in the acidic media. The pK_a of 4-NP is 7.15, thus it is negatively charged at pH values greater than 8 and neutral below pH 6 [7]. This can be Explained on the basis of surface charge of ZnO and hydrophobicity of HZSM-5.

In figure 6, is reported which confirm that acidic media has high efficiency in degradation 4-nitro phenol.

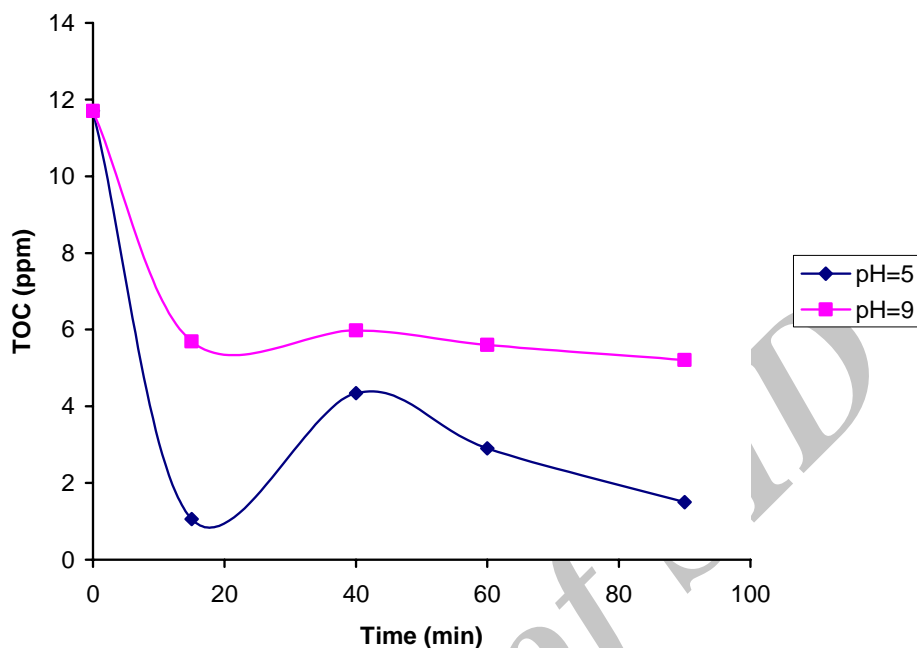


Figure6. TOC concentration of degradation of 4-nitrophenol on ZnO/HZSM-5 7% loading amount versus irradiation time at different pH

Based on the previous findings, a tentative reaction pathway for mineralizing NPs to CO_2 is presented in Fig7. In this processes, the main oxidizing species is $\bullet OH$ radical, which initiates the degradation process. Hydroxyl radical has a strong electrophilic character, and attacks one of the carbon atoms of the aromatic ring with highest electron density. The attack of electrophilic $\bullet OH$ radical occurs at ring position activated by the presence of two substituents in NPs, namely hydroxyl (OH) and nitro (NO_2) group. The electron-donating substituent, phenolic OH group, increases the electron density at ortho and para positions, while electron-withdrawing substituent, NO_2 group, is strongly deactivating and meta-directing. Figure 5 shows Possible oxidation pathways of 4-NPh [9].

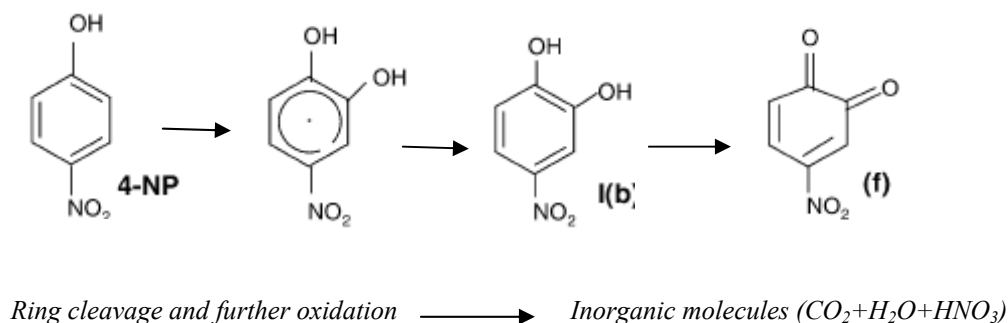


Figure 7. Possible oxidation pathways of 4-NPh

Conclusion

At low ZnO loading, no diffraction peak of macrocrystalline ZnO exists. At high ZnO loading, the diffraction peaks of ZnO with wurtzite structure appear and develop with increasing loading. At high ZnO loading, ZnO particles covered the extra surface of HZSM-5. ZnO encapsulated inside HZSM-5 have high efficiency in photodegradation of 4-nitrophenol. ZnO/HZSM-5 with 7% loading amount has high surface area of zeolite which enhances adsorption as well as degradation of 4-nitrophenol.

References

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