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Degradation of 4-nitrophenol (4-NP) using ZnO nanoparticles supported on zeolites and modeling of experimental results by artificial neural networks

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ABSTRACT

In this paper, we report the synthesis of ZnO, ZnO/HZSM-5, ZnO/HY and ZnO/Clin by a poly acrylamide pyrolysis method for the first time. The presences of carbon network/cages in the poly acrylamide gel can effectively prevent particle agglomeration. The catalytic activity of all specimens was tested by carrying out the 4-nitrophenol degradation, used as a "probe" reaction, in the aqueous medium under ambient visible light. The prepared samples were characterized by X-ray diffraction (XRD), specific surface area (BET) and porosity determination, scanning electron microscopy (SEM) coupled with energy dispersive X-ray analysis (EDX), visible-ultraviolet diffuse reflectance spectroscopy (DRS) and Fourier transform infrared spectroscopy (FT-IR), to evaluate particle structure, size distribution and composition. The results revealed that among the catalysts, ZnO/HZSM-5 showed higher percentage of adsorption than others. The time required for complete mineralization of 4-NP under ambient visible light over ZnO/HZSM-5 was 75 min. The higher activity of ZnO/HZSM-5 is mainly due to fine dispersion of ZnO and hydrophobicity of the support. An artificial neural networks (ANNs) model was developed to predict the performance of catalytic degradation process over synthesized catalysts based on experimental data. A comparison between the predicted results of the designed ANN model and experimental data was also conducted.

1. Introduction

Wide band semiconductors have been the focus of modern research in many areas, such as catalysis [1,2], optical sensitizers, photocatalysts [3], gas sensors [4,5], ceramics [6], and exhibiting photoluminescence gain and lasing effect, etc. In particular, Zinc Oxide, a wide band-gap semiconductor (gap = 3.37 eV, 298 K) [7], shows significant quantum size effect (QSE) when its size reaches to nanometer scales [8,9]. Catalytic materials exist in various forms and their preparation involves different protocols with a multitude of possible preparation schemes, many times larger than the number of known catalysts. Moreover, preparation of any catalyst involves a sequence of several complex processes, many of them not completely understood. Until now, various methods have been employed to prepare ZnO nanoparticles with extremely small diameters including precipitation of colloids in solution [10], sol–gel methods [11,12], thermal decomposition methods [13], pulsed laser deposition (PLD) [14] and metal-organic chemical vapor deposition (MOCVD) [15]. However, in general it is very difficult to avoid the aggregation of ZnO nanoparticles during the preparation. This work aims to resolve this problem via the growth of ZnO nanoparticles inside the channels of a porous matrix such as zeolite. Zeolites are crystalline nano porous materials possessing interconnected Channels those are accessible to molecules of suitable size. Diversity in pore size, shape, topology, and framework composition provides zeolites as a rich variety of interesting properties and industrial applications such as catalysts, ion exchangers, and adsorbents [16]. The goal of a catalyst manufacturer is to produce and reproduce a stable, active, and selective catalyst. To achieve this goal, the best preparative solution is sought which results in sufficiently high surface area, good porosity, and suitable mechanical strength. The first of these, surface area, is an essential requirement in that reactants should be accessible to a maximum number of active sites.

In recent years, modeling of nonlinear systems using neural networks and their application in control strategies have been fairly widespread and found to yield good results. It has been shown by researchers using the universal approximation theorem that these networks, if properly developed and trained, can approximate any nonlinear continuous function arbitrarily accurately. Artificial neural networks have also been widely applied in various control strategies. These networks approximate the function mapping from system inputs to outputs, given a set of observations of inputs and corresponding outputs, by adjusting its internal parameters, i.e., weights and biases, to minimize the squared error between the network's outputs and the desired outputs. The use of neural

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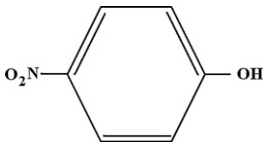

Scheme 1. Structure of 4-NP.

networks to model uncertain nonlinear functions within the geometric control technique has been demonstrated by several researchers [17,18].

In the present paper, hosts of micro porous aluminosilicate such as HZSM-5(MFI type), Clinoptilolite (HEU type) and zeolite HY(FAU type) are used to encapsulate ZnO clusters by using poly acryl amide pyrolysis method and their photocatalytic activities are tested for degradation of 4-NP (Scheme 1) for the first time. An artificial neural networks (ANNs) model was developed to predict the performance of catalytic degradation process over synthesized catalysts based on experimental data. A comparison between the predicted results of the designed ANN model and experimental data was also conducted.

2. Experimental

2.1. Materials

HZSM-5 (Si/Al = 58.37) zeolite was synthesized in our laboratory [19]. A commercial Y type zeolite (Si/Al = 4) was provided by VOP ($429\ m^2\ g^{-1}$). And the local Clinoptilolite (Si/Al = 9.53) was used. Zinc acetate dihydrate, nitric acid, citric acid, acryl amide, 2,2′-azoisobutyronitrile (AIBN) were obtained from Merck.

For convenience, we call commercial Y type zeolite and local Clinoptilolite as HY and Clin in this paper.

2.2. Measurements

X-ray diffraction patterns (XRD) were collected using a Siemens D500 diffractometer with Cu kα radiation ($\lambda = 1.5418$ A and $\theta = 4$–80°) at room temperature. FT-IR spectra were obtained with a Bruker Tensor 27 Fourier Transform Infrared spectrometer with the KBr pellet technique. UV–Vis diffuse reflectance spectra (UV–Vis DRS) were recorded in air at room temperature in wavelength range of 200–800 nm using a Scinco 4100 spectrophotometer. The band gap energy was calculated by the following equation:

$$\lambda_g = \frac{1240}{E_g},$$

where λ_g is the wavelength of the characteristic absorption peak value; E_g is the band gap energy.

Scanning electron microscope (Philips XL30) equipped with energy dispersive X-ray (EDX) facility was used to capture SEM images and to perform elemental analysis. The SEM sample was gold coated prior to examination and SEM was operated at 5 kV while EDX analysis was performed at 15 kV. The Brunauer–Emett–Teller (BET) surface area of the catalysts was measured by N2 adsorption–desorption isotherm at liquid nitrogen temperature using NOVA2000 (Quantachrome, USA).

2.3. ANN software

All ANN calculations carried out using Mat lab 7.8.0 mathematical software with ANN toolbox. In this study, a three-layer network with a sigmoidal transfer function (trainscg) with back propagation algorithm was designed.

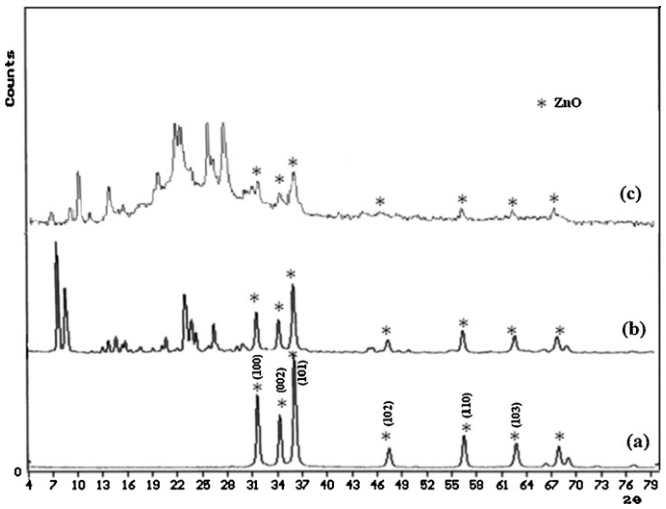

Fig. 1. The XRD patterns of: (a) ZnO, (b) ZnO/HZSM-5, (c) ZnO/Clin.

2.4. Nanocomposite preparation

In this work ZnO clusters by using poly acrylamide pyrolysis was synthesized by the following four steps reaction:

Step 1: 0.17 g (0.774 mmol) $Zn(CH_3CHOO)_2{\cdot}2H_2O$ was dissolved in 2 ml dilute nitric acid ($2\ mol\ L^{-1}$) and 0.3 g citric acid(1.6 mmol) was added in order to accelerate dissolution of $Zn(CH_3CHOO)_2{\cdot}2H_2O$. The mixture were kept stirring for 2 h. The final PH was controlled as 6–7 by using dilute ammonia (solution A).

Step 2: Subsequently, the monomers of acrylamide (0.3 g) were added into the clear solution A. The resulting solution was stirred for 20 minutes (solution B).

Step 3: The solution B was heated in a water bath and during the whole process, the system was continuously stirred. The solution became gradually transparent with temperature rising. When the temperature reached about 80 °C, a small amount of compound initiator AIBN ($C_8H_{12}N_4$) was added into the solution and polymerization occurred quickly and transparent polymeric resin was obtained without any precipitation.

Step 4: At last, the gel was dried at 100 °C for 24 h to yield a xerogel. The xerogel was heated in a laboratory furnace at 300 °C for 10 h to burn out the organic residues and calcined at higher temperature (500 °C) for 5 h.

For the preparation of ZnO/HZSM-5, ZnO/Clin, ZnO/HY nano composites, after second step of preparing ZnO clusters, the resulting solution B was added to 0.5 g of each zeolite and stirred for 30 min and then third and fourth step were done.

3. Results and discussion

3.1. Catalysts characterization

3.1.1. XRD analysis

The XRD patterns of pure ZnO, ZnO/HZSM-5, and ZnO/Clin, prepared by P.S.M. at the same calcinated temperature (500 °C) are shown in Fig. 1. The diffraction peaks for ZnO were in good agreement with those given in the standard data (PCPDF, 79-0207) and showed a good crystallinity. This means that as prepared materials had crystallized in a hexagonal wortzite ZnO (see Table 1). On the other hand, it is clear to see that the width of the reflections is considerably broadened, indicating that a small crystalline domain size. The average crystallite size of nano ZnO was determined as