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A study of the effect of microwave treatment on metal zeolites and their use as photocatalysts toward naptalam

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ABSTRACT

A new route to fabricate silver and gold-based material incorporated into the Y zeolite framework is reported. X-ray fluorescence (XRF), X-ray photoelectron spectroscopy (XPS), UV–vis diffuse reflectance, and low-temperature steady-state photoluminescence spectroscopic results indicate the formation of metallic silver and gold as well as ionic clusters on the zeolite framework. Microwave treatment affects the surface morphology and the metal content of different catalyst systems. The photodecomposition of the pesticide naptalam is enhanced in the presence of silver and gold exchanged into zeolite Y catalysts. The largest catalytic activity was observed for the AgAuYm catalyst where an increase in the decomposition rate by 20-fold was observed compared to the uncatalyzed irradiated naptalam solution. While the microwave treated mixed sample (Ag-AuYm) acts as a good catalyst for the degradation of naptalam, the untreated sample (Ag-AuY) provides a selective surface that completely adsorbs naptalam from solution. GC–MS, HPLC, and synchronous scan luminescence spectra (SSLS) results show the formation of three products namely, α-naphthylamine, phthalic acid, and N-1-naphthylphthalimide for the photodecomposition of naptalam irradiated at 254 nm in aqueous solution. This is in contrast to the catalyzed reactions where N-1-naphthylphthalimide is the major product.

1. Introduction

Human health is threatened by the use of large amounts of pesticides for food production, as well as by chemical warfare agents. This makes it important to eradicate the danger of these pollutants to humans. For example, naptalam and its derivatives are pesticides used in agriculture for the protection of cucumbers, melons, pumpkins, groundnuts and soybeans crops. Studies have indicated that people could be exposed to naptalam by consuming food products or from water resources. The United States Environmental Protection Agency (USEPA) has stated that risk-reduction measures should be implemented to make naptalam incapable to affect human health [1]. It is non-toxic to freshwater fish and invertebrates but toxic to small mammals on an acute oral basis. Since naptalam is a widely used pesticide, it is found to be adsorbed by seeds and primary roots of weeds and is very mobile in fine sands or a silt loam soil [2,3]. As a result, it is important to develop materials to decontaminate this pollutant from water sources.

Because of their definite pore and channel structures, zeolites have been used in several industrial applications such as ion-exchangers, molecular sieves, sorbents, photocatalysts, as well as the petroleum industry [4–17]. In specific, the field of transition metal/zeolite chemistry has been advanced with synthetic a development in which partial oxidation of hydrocarbons with high selectivity is achieved by using metal anchored zeolite catalysts [18–21]. In order to introduce a transition metal into zeolites, hydrothermal methods, photosynthetic methods, cation exchangeable sites with a conventional ion-exchange method, or γ- or X-ray irradiation can be used [22–26]. Using a cation exchange strategy, we recently prepared different silver nanoclusters, as well as dicyanoargentate and dicyanoaurate nanoclusters doped in zeolites A, Y, and ZSM-5 [10–17]. Silver and gold clusters are favored because of their chemical stability and high catalytic activity under various conditions. Therefore, new catalysts have been prepared by the application of various inorganic salts or metal oxides with different types of zeolite. For example, silver ions with various sizes such as Ag_2^+, Ag_2, Ag_3^{2+}, and Ag_6^{4+} have been identified in zeolite Y [27–30]. Moreover, transition metals doped in zeolites have been found to show good catalytic activity toward several organic pollutants due to their high surface area and their channel-like

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structures [31–36]. In this paper we report for the first time that the photocatalysis of naptalam with the microwave treated zeolites is superior to the untreated microwave catalysts.

2. Experimental.

2.1. Instrumentation

Microwave digestion was done using QLAB 6000 from Questron Technologies Corp. The temperature of the vessels reached 190 °C and was held for 30 min.

Reflectance spectra were recorded by an Ocean Optics usb4000 spectrometer coupled to halogen and helium arc lamps via a fiber optic probe with Y zeolite being used as a blank. Steady-state photoluminescence spectra were recorded with a Model QuantaMaster-1046 photoluminescence spectrophotometer from Photon Technology International (PTI). The instrument is equipped with two excitation monochromators and a single emission monochromator. Photodecomposition of naptalam was monitored using a Varian fluorescence spectrometer. X-ray fluorescence spectra (XRF) were recorded with an X-ray analytical microscope XGT-7200 Horiba Scientific. X-ray photoelectron spectroscopy (XPS) measurements were conducted using an Omicron ESCA probe spectrometer with unmonochromatized Mg Kα X-ray with an energy of 1253.6. The samples were spotted as drop-cast films on a sample stub. A constant analyzer energy of 20 eV was used for the measurements. The pass energy was 50 eV for survey scans and 20 eV for specific regions. Finally, the silver loadings were analyzed with an ICP Perkin-Elmer Optima having a radio frequency (RF) power of 1300 W.

Surface area measurements were performed via a methylene blue (MB) adsorption method [37]. In brief, a calibration curve was made by using various MB concentrations from 0.07 to 7.0 ppm (diluted from 0.5000 g of MB, dissolve in 100 mL of distilled water stock solution). The absorbance of the above solutions was recorded at $\lambda_{\max} = 665$ nm and used to make a calibration curve. A 0.1000 g powder sample was mixed with 100.0 mL of distilled water then different volumes ranges from 0.1 to 3.5 mL of the above MB stock solution were added. The final solutions were mixed continuously at room temperature for 2 h at 200 rpm and then settled overnight. After that, 5.0 mL of the solution was treated by centrifuge and the absorbance for the residual clear solution was measured. The surface areas were then calculated using Eq. (1)

$$S_s = \left(\frac{m_{MB}}{319.87}\right) A_v A_{MB} \left(\frac{1}{m_s}\right) \tag{1}$$

where m_{MB} is the mass of the absorbed MB at the point of complete cation replacement, A_v is Avogadros' number, A_{MB} is the area covered by one MB molecule, and m_s is the mass of the zeolite specimen.

High performance liquid chromatography (HPLC) measurements were performed with an Agilent 1100 series high performance liquid chromatograph equipped with an operating software Chemstation for LC 3D with a diode-array detector. Separations were made on a Zorbax Eclipse XDB-C8 column, with a dimension of 150 mm × 4.6 mm and a particle size of 5 μm. The flow rate was 1 mL/min for all experiments. The mobile phase used was 80% acetonitrile, 20% of 0.1 M acetic acid solution at pH 3.0. The detector was set to monitor at 220 nm.

Gas chromatography–mass spectrophotometry (GC–MS) was used to identify the products of irradiated naptalam. The measurements were taken on a variant CP-3800 gas chromatograph with a Varian Saturn 2000 GC/MS/MS serving as a detector. A 30 m × 0.25 mm column was used. The various components of the sample were separated with an injector temperature set at 150 °C. Initially the oven temperature was set at 70 °C and held for 1 min. Then the temperature was increased to 280 °C at a rate of 10 °C/min and held for 25 min.

2.2. Irradiation of naptalam

A 30 ppm stock solution of naptalam was prepared in a 10:90% (v:v) methanol:water mixture. All irradiations were performed with a 254 nm UV lamp (model UVS-28) from VWR Scientific, Inc. The relative intensity of the lamp is 1300 $\mu W/cm^2$ at 3 in. Each sample was irradiated in quartz test tubes that have an inside diameter of 12.5 mm, a length of 10 mm, and 1 mm wall thickness. Only one test tube was irradiated at a time. The naptalam solutions were prepared and exposed to UV light at a distance of 3.0 in., where a maximum output of the lamp was reached.

Relative fluorescence quantum yields were determined for naptalam solutions irradiated for 90 min in the presence and the absence of the catalysts. The fluorescence and the absorbance spectra of each irradiated sample as well as a standard reference tryptophan solution were recorded. The quantum yields were then calculated using Eq. (2):

$$\Phi = \Phi_R \times \frac{Int_R}{Int_R} \frac{A_R}{A} \frac{n^2}{n_{R^2}} \tag{2}$$

Here Φ is the quantum yield, *Int* is the area under the emission peak, *A* is absorbance at the excitation wavelength, and *n* is the refractive index of the sample. The subscript *R* denotes the respective values of the tryptophan reference solution.

2.3. Preparation of the zeolite based catalysts

Zeolite Y was encapsulated with different metals under various conditions. Two sets of samples containing silver, gold, and mixed silver-gold nanoclusters were synthesized. One set was prepared using a normal cation exchange procedure (labeled AgY, AuY, and Ag-AuY) while the second set was treated with a microwave digestion process (referred to as AgYm, AuYm, and Ag-AuYm). For preparing AgYm and AgY, 2.0 g of Zeolite-Y was taken with 40.0 mL of 2.0 M $AgNO_3$ in 5.0 mL ammonia mixed with 2.0 mL of acetaldehyde. Finally, this 40.0 mL solution was divided into two sets of 20.0 mL. One set was taken for microwave digestion, where 1.0 mL of concentrated nitric acid was added and the temperature was increased by 190 °C for 30 min and then with constant stirring for 24 h at room temperature. The other 20.0 mL solution was stirred for 24 h at 75 °C. Both solutions were calcined at 350 °C for 3 h. A similar protocol was applied for the pure gold samples with a 2.0 M solution of $AuCl(PEt_3)$ being used as the source for gold. Moreover, for the Ag-AuY and Ag-AuYm samples, 40 mL of $AgNO_3$ and ammonia combined with acetaldehyde mixed with zeolite and $AuCl(PEt_3)$ in a methanol:water solution. In a similar pattern, 20.0 mL was taken for microwave digestion and another 20.0 mL for stirring and evaporation. All samples were aged for 24 h at 75 °C and then calcined at 350 °C for 3 h with a gradual increase in temperature by 10 °C/min.

3. Results and discussion

Silver, gold, and mixed silver-gold nanoclusters doped into zeolite Y were prepared with and without the microwave digestion protocol as described earlier. The samples were analyzed using X-ray fluorescence, Inductively coupled plasma, X-ray photoelectron spectroscopy, UV–vis reflectance, and steady-state photoluminescence techniques. In addition, the surface area for all samples was measured using a methylene blue adsorption protocol.

X-ray fluorescence data indicate the presence of silver and gold, along with the zeolitic silicon and aluminum primary lines (K-lines). Fig. 1 shows the XRF spectra for the AgY, AuY, and Ag-AuY