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Chromium oxide loaded silica aerogels: Novel visible light photocatalytic materials for environmental remediation

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ABSTRACT

Various photocatalytic systems have been reported for degradation of harmful air pollutants. Most of the reported catalysts are based on well-known semiconducting material, titanium dioxide (TiO_2), while some are based on other materials such as silicon dioxide (SiO_2), various zeolites. However, titania based systems are very popular in this regard and the most of the photocatalytic processes that involve titania are considered non-localized.

Thus, to study the photocatalytic ability of a localized system, novel aerogel based samples were studied using silica and chromium and tested for photocatalytic activities. The new photocatalytic systems were prepared to obtain aerogel silica as the matrix material by co-hydrolyzing silica precursor with chromium(III) ions to obtain chromium loaded silica materials. Later, these prepared samples were compared to chromium loaded titania and mixed TiO_2–SiO_2 systems. All the prepared systems have high surface areas compared to the systems that have been reported in literature. Samples were characterized by X-ray diffraction, diffusive reflectance UV spectroscopy, and BET surface analysis methods. The kinetics of photocatalytic degradation of a model pollutant, acetaldehyde, was performed using a Shimadzu GCMS-QP 5000 instrument and a glass reactor with a quartz window.

Change in photocatalytic activity was found with various molar ratios of SiO_2 to TiO_2. From all the systems, chromium loaded pure SiO_2 showed the highest activity towards acetaldehyde degradation compared to mixed TiO_2–SiO_2 systems and TiO_2 based systems. The interesting photocatalytic activity of silica based materials occurs due to the efficient insertion of chromium ions into silica matrix to generate reactive sites. The photo excitation is believed to occur at molecular orbital level at localized chromium sites.

1. Introduction

Photocatalysis has been studied actively during the past several decades because of its application to green energy and due to the understanding of the importance of a cleaner atmosphere. As a result there are a large number of reports about applications of photocatalysis in various tasks such as environmental remediation, photocatalytic water splitting, etc. Photocatalysis has widely been studied to destroy organic dye compounds from industrial effluents, oxidation of indoor and outdoor organic pollutants, etc. The basic advantage of photocatalysis is its ability to mineralize a large variety of harmful organic pollutants under ambient temperature and pressure conditions [1].

In most of the successful photocatalytic materials that have been reported earlier a supporting base material is used. Titania is the most widely used photocatalytic material that has shown success in organic material decomposition. It is believed that the supporting material facilitates the catalytic activity of the catalytic site by enhancing charge carrier separation, allowing reduced electron–hole recombination and facilitating charge transfer to adsorbed species making photocatalytic processes are non-localized [2–4]. But, whether a photocatalytic process must always be non-localized and semiconductors are required are questions that still needs to be answered.

Therefore, our main objective is to discover photocatalytic systems which progress according to localized mechanisms. The study was carried out by preparing such a system using insulating silica materials. Generally low reactivity and higher band gap energy of silica makes it a suitable material to study the localized properties of photocatalysis.

Furthermore, to achieve visible light activity, it is important to insert a suitable light harvesting material into silica in order to introduce photocatalytic activities. Transition metals and metal oxides have been actively used in this regard. Transition metals are very good candidates to absorb in the visible range of the spectrum,

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as orbital energy transfer usually lies in the visible range. According to several literature reports and based experiments which were carried out in our lab, chromium loaded systems showed highest activities towards oxidation of organic air pollutants. Thus, for our systems chromium was chosen as the doping agent for our more in-depth study of Cr–SiO_2 and mixed TiO_2–SiO_2 samples [5–8]. Herein we report the observed UV and visible light activities of chromium ions loaded silica and titania based materials and possible mechanisms for the observed photocatalytic performances.

2. Material and methods

2.1. Photocatalyst preparation

2.1.1. Preparation of chromium ions loaded silica and/or titania aerogel samples

Chromium ion loaded silicon dioxide (silica), titanium dioxide (titania) and mixed TiO_2–SiO_2 samples with varying molar ratios of silica to titania were prepared using an aerogel preparation method. During the synthesis process tetraethylorthosilicate (TEOS) and titaniumisopropoxide ($Ti(ipr)_4$) were used as corresponding silica and titania precursors respectively. These precursors were co-hydrolyzed in the presence of chromium(III) nitrate ($Cr(NO_3)_3 \cdot 9H_2O$), which is the chromium ion precursor. All the chemicals were analytical grade used without further purification. During the preparation of samples an amount equivalent to 0.1 mol% of the dopant material was dissolved in 140 ml of methanol and 20.0 ml of TEOS solution and stirred well. Corresponding titania based samples were prepared using the same amount of chromium(III) nitrate dissolved in 140 ml of methanol and 26.6 ml of $Ti(ipr)_4$ mixed TiO_2–SiO_2 samples were prepared using corresponding silica and titania precursor amounts for the molar ratios expected for the final products. Then, a mixture of 0.5 ml of water and 2.5 ml concentrated nitric acid was added drop wise to hydrolyze silica and/or titania precursors. The solution mixture was then aged for about 15 min and super critical drying was carried out in an autoclave. Then the autoclave was quickly vented soon after the temperature reached 265 °C. Finally, the resulting powder was calcined in air at 500 °C for 2 h.

2.2. Kinetic studies of photocatalytic systems

Prepared samples were tested for both UV light and visible light photocatalytic activities. Kinetics of the photocatalytic degradation was studied using a Shimadzu GCMS-QP 5000 instrument and a glass reactor with a quartz window. Acetaldehyde was used as a model pollutant and the temperature of the glass reactor was maintained at 25 °C by circulating water in the outer jacket of the reactor during all the kinetic experiments. In a typical experiment 0.10 g of the prepared sample was uniformly placed on the special glass chamber allowing UV (320 nm–400 nm) or visible light ($\lambda > 420$ nm) to directly contact the prepared photocatalytic material. Then the air filled system was sealed and 0.10 ml of liquid acetaldehyde was introduced to the bottom of the reactor to avoid any direct contact of liquid acetaldehyde and the photocatalytic material. During the experiment acetaldehyde slowly gets evaporated due to its near room temperature boiling point, and gaseous acetaldehyde gets absorbed on to the reaction sites of the catalyst. Photocatalysts were then illuminated with UV or visible light using a 1000 W xenon lamp and glass filters by cutting off unnecessary light. The progress of any reaction was detected by injecting 35 μl of gas samples from the sealed reactor to the Shimadzu GCMS-QP 5000 instrument every 20 min. All the kinetics experiments were carried out at least two times in order to confirm the accuracy of the results and were compared with commercially available titania P25 and prepared blank samples, where no dopant elements were present.

2.3. Characterization studies

Brunauer–Emmet–Teller (BET) measurements of surface area and pore size distribution of the prepared samples were determined using a Quantachrome NOVA 1200 gas absorption/desorption analyzer after degassing the samples at 150 °C for 2 h. Powder XRD analysis of the samples was carried out to determine the crystalline nature using a Scintag-XDS-2000 spectrometer with Cu Kα radiation with applied voltage of 40 kV and current of 40 mA. Samples were scanned 2θ from 0° to 75° with a scan rate of 1° per minute. Diffuse reflectance UV–visible spectra were measured at room temperature in air on a Cary 500 scan UV–vis–NIR photometer over the range from 200 to 900 nm. The sample cell was made of two transparent CaF_2 discs, a Teflon O-ring and screw-type combination in which photocatalysts were packed between two discs and the O-ring. Polytetrafluoroethylene (PTFE) powder of 1 μm particle size was taken as a reference material for diffuse reflectance studies.

The compositions of prepared photocatalysts were determined by carrying out elemental analysis using energy dispersive spectrometry using a scanning electron microscope. Detailed study of the loaded chromium was carried out using a bulk elemental analysis to determine the final amounts of loaded ions. Bulk elemental analysis was carried out using simultaneous optical systems and axial or radial viewing of the plasma using Perkin Elmer Optima 5300 spectrometer at Galbraith Laboratories Inc.

TEM studies were carried out using a Philips CM100 operating at 100 kV. The TEM samples were prepared by dispersing few milligrams of the catalyst in ethanol using an ultrasonic bath. Then a drop of catalyst–ethanol mixture was placed on the TEM grid and air dried. The facilities were provided by the Microscopy and Analytical Imaging Laboratory at Department of Biology, Kansas State University.

2.4. Hydroxyl radical generation studies using terephthalic acid

Terephthalic acid (TPA), which is not a fluorescent compound, gives a single, fluorescent product, 2-hydroxyterephthalic acid (HTPA), by reacting with hydroxyl radicals produced during the photocatalytic reaction (Fig. 1). HTPA emits fluorescence at around 426 nm on the excitation of its own 312 nm absorption band. The measurements of the amount of $OH^{\bullet}$ were performed for the chromium loaded titania and silica based systems carrying out photocatalytic reaction by means of this TPA fluorescence probe method as follows. For the measurements of any hydroxyl radicals generated during photocatalytic reactions the photocatalyst samples were irradiated under UV and visible light in terephthalic acid solution (2×10^{-3} M). Then the solution, after separation from the photocatalyst, was taken for fluorescence analysis. The fluorescence measurements were carried out at the excitation wavelength of 314 nm in the range of emission wavelength from 330 nm to 600 nm with maximum peak at 425 nm [9–11].

3. Results and discussion

3.1. Structure of chromium loaded photocatalytic systems

It is well-known that the effective surface area of a material is important in deciding the photocatalytic efficiency of a material because in most of the photocatalytic systems the catalytic activity takes place on the surface of the material [12]. Therefore, the photocatalyst synthesis process was specially designed to obtain higher effective surface area using a super critical drying technique.