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Aerogel materials for photocatalytic detoxification of cyanide wastes in water

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Abstract

Ultraviolet-irradiated titania–silica (TiO_2–SiO_2) aerogels were used as photocatalysts to oxidize/degrade aqueous cyanide species to CO_2 and N_2. TiO_2–SiO_2 aerogel photocatalysts were prepared by the sol–gel technique and supercritical drying. Three types of TiO_2–SiO_2 aerogel were prepared with different SiO_2 contents (i.e., $TiO_2 : SiO_2$ molar ratio = 1 : 1.3, 1 : 2.6 and 1 : 3.9). It was observed that, with increased SiO_2 content, shrinkage and apparent density decreased and translucency increased. This resulted in higher photocatalytic activity for oxidation of CN^- in dilute solutions (1000 and 522 ppm) of ferric cyanide. Compared with titania powder (i.e., anatase form with $TiO_2 > 98\%$ and particle diameter < 1 μm), it was proven that the aerogel with highest SiO_2 content (i.e. $TiO_2 : SiO_2$ molar ratio = 1 : 3.9) had highest efficiency in the photocatalytic oxidation of CN^- species under the same experimental conditions. This aerogel photocatalyst was filtered and re-used several times to check for activity loss; no significant change in the activity of the photocatalyst was observed.

1. Introduction

Hazardous industrial aqueous wastes containing free and complexed cyanides are generated in large volumes in metal finishing industries including electroplating and heat-treating operations [1,2]. Unit processes typically used for treatment of these cyanide wastes are: alkaline chlorination, electrolytic oxidation, ozonation and, to a lesser extent, wet air oxidation and ion exchange. Currently, alkaline chlorination is the best available proven technique for the treatment process [2,3]. However, this cyanide waste treatment technique has two important limitations. First, only the free cyanide species are oxidized into nitrogen and carbon dioxide leaving behind the complex metal cyanides in sludge. The sludge thus formed has to be disposed of as hazardous solid waste, usually in a landfill. Second, a highly toxic (as toxic as hydrogen cyanide) cyanogen chloride gas can be formed and released during the treatment process.

Recent investigations showed that semiconductor powders, such as titanium dioxide (anatase), suspended in solution can utilize solar energy for photocatalytic oxidation of cyanide [3–6]. Irradiation of a TiO_2 particle with ultraviolet (UV) light of wavelengths of 300–400 nm, from either a xenon light or unfocused sunlight, causes excitation of an electron (e^-) to the conduction band leaving a hole (h^+) in the valence band. Apparently these electrons and holes can be trapped in surface levels with recombination being sufficiently slow that the electron trans-

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fer process can occur. The conduction band electrons reduce oxygen while the valence band holes cause the oxidation of CN^-. Thus the process of removal of CN^- can be represented as

$$TiO_2 + 2h\nu = TiO_2(2h^+ + 2e^-)\text{surface}$$

$$0.5O_2 + 2\ e^- + H_2O = 2OH^-$$

$$2OH^- + 2h^+ = 2OH\cdot$$

$$CN^- + 2OH\cdot\ = OCN^- + H_2O$$

$$2OCN^- + O_2 = 2CO_2 + N_2$$

Overall reaction:

$$2CN^- + 2O_2 + (h\nu) = 2CO_2 + N_2,$$

where h is Plank's constant and ν is the frequency [7].

As the photocatalytic oxidation reaction takes place at the interface between the solution containing cyanide species and the semiconductor titania, the rate of oxidation will depend on the surface area of the semiconductor. Therefore, colloidal titania sol was used [3]. However, the main disadvantage of using colloidal titania is the difficulty of recovering all titania used after the treatment process, i.e., the effluent stream will be contaminated with titania powder.

Alternative methods for synthesizing colloidal titania semiconductor aggregates involve the use of solid matrices such as porous glasses [8]. The size and shape of the semiconductor are determined in this case by the morphology and texture of the microscopic voids of the host template where aggregation occurs. The novel concept described in this work is to use the sol–gel technique to prepare TiO_2 photocatalyst in the form of TiO_2–SiO_2 aerogel materials (porous and translucent matrices). Such aerogel materials can have > 90% porosity, very low density and extremely high surface area, currently several hundred m^2/g and a pore diameter distribution extending from nm to μm range [9]. So, the primary objective of this work was to determine whether the TiO_2–SiO_2 aerogel samples prepared in the laboratory can profitably be used for photo-catalytic oxidation of CN^- in dilute solutions of ferric cyanide. Once this has been realized, research will continue to refine the aerogel preparation and to optimize the photocatalyzed oxidation process.

2. Experimental procedures

In the first two series of tests, two different titanium dioxide powders were used. The first powder ($TiO_2 > 98\%$) had a particle diameter < 1 μm and the crystal structure was primarily anatase. In the second series of tests rutile ($TiO_2 = 93.3\%$) with a particle diameter < 200 μm was used.

In the other three series of experiments, TiO_2–SiO_2 aerogels (with different $TiO_2:SiO_2$ molar ratios) were used. The tested aerogels were manufactured by preparing the corresponding alcogels using the sol–gel processing technology, then by supercritical drying to remove the alcohol.

In the present work, three different samples of TiO_2–SiO_2 alcogels were prepared with different concentrations. The compositional $TiO_2:SiO_2$ molar ratios were 1 : 1.3, 1 : 2.6 and 1 : 3.9 (i.e., 1 : 1, 1 : 2 and 1 : 3 wt ratio), respectively. All gels were synthesized by hydrolysis and polycondensation reactions of organometallic compounds. Tetraethylorthosilicate ($Si(OC_2H_5)_4$) and titanium isopropoxide ($Ti(OC_3H_7)_4$) were used as sources of SiO_2 and TiO_2 respectively. Gelation took place in the presence of ethanol (C_2H_5OH) which is readily soluble with the organometallic compounds and the distilled water used for hydrolysis. Nitric acid (HNO_3) was used as a catalyst. Details of the process used to prepare the appropriate alkoxide solution of TiO_2–SiO_2 are published elsewhere [10,11]. Fig. 1 shows a flowchart of the sol–gel procedure used.

Drying of the TiO_2–SiO_2 gels was carried out under supercritical conditions. For ethyl alcohol, supercritical conditions are 243°C and 63.6 bar [10]. For this reason, the gels were introduced to an autoclave with excess amount of alcohol to attain a pressure higher than the critical pressure at the critical temperature. After tightly closing, the autoclave was flushed with 2 bar dry N_2 twice and finally pre-pressurized up to about 10 bar N_2. The temperature of the autoclave was increased, at a rate of 1.0–0.5°C/min, to a temperature of about 280°C. The pressure in the autoclave increased to about 110 bar. After stabilizing the maximum temperature and pressure for about 3 h, the vapor outlet micrometering valve of the autoclave was slowly opened to vent out the solvent to the condenser. All the solvent from the autoclave was evacuated in 3–4 h at a constant

Table 1
Experimental photocatalysts used in the oxidation of CN^- species

Photocatalyst	Characteristics
Aerogel 1	$TiO_2 : SiO_2$ molar ratio = 1 : 3.9, grain size < 3 mm
Aerogel 2	$TiO_2 : SiO_2$ molar ratio = 1 : 2.6, grain size < 3 mm
Aerogel 3	$TiO_2 : SiO_2$ molar ratio = 1 : 1.3, grain size < 3 mm
Anatase (powder)	$TiO_2 > 98\%$, particle diameter < 1 μm
Rutile (powder)	$TiO_2 = 93.3\%$, particle diameter < 200 μm

temperature of about 280°C. After reaching atmospheric pressure, in order to remove the trapped solvent vapor molecules, heating was continued for about 20 min and finally the autoclave was flushed twice with 2 bar N_2. During this treatment, condensation of the outlet solvent vapor on the walls (pyrex glass) of the condenser was clearly seen. The aerogels were then heat-treated in air at about 650°C for about 5 h.

The TiO_2–SiO_2 aerogels were characterized by measuring the linear and volume shrinkage and determining the apparent density.

The linear (diametrical) and volume shrinkage, L/L_0 and V/V_0, respectively, were measured for each aerogel sample after drying by applying the following relations [12]:

$$L/L_0 = (L_0 - L)/L_0$$

$$V/V_0 = (V_0 - V)/V_0,$$

where L_0 and V_0 are the diameter and volume of the alcogel (i.e., before supercritical drying) and L and V after supercritical drying.

The density of the aerogels could not be determined by the normal Archimedes method because of the porosity of aerogels. The density, ρ_{aerogel}, was, therefore, determined by applying the following relation [13]:

$$\rho_{\text{aerogel}} = 0.997 M_a/(M_0 - M_w) \text{ g/cm}^3,$$

where M_a is the weight of the aerogel sample in air (dry weight), M_0 is the weight of the aerogel sample after immersion in a hydrophobic oil for several hours, M_w is the weight of the aerogel sample in water with filled pores by oil and 0.997 is the density of water (g/cm^3) at 25°C.

Dilute solutions (1000 and 522 ppm) of ferric cyanide, one of the most common species present in industrial cyanide wastes, were used in this investigation as a synthetic cyanide waste.

All experiments consisted of illuminating about 300 ml of the cyanide solution in a reactor (pyrex glass) containing the photocatalyst. The photocatalyst loading was maintained constant at 1.0 wt% TiO_2 in the form of powders, i.e., anatase and rutile, or granules, i.e., TiO_2–SiO_2 aerogels, as given in Table 1. The photocatalyst was kept in suspension by bubbling air through the solution during the entire reaction process. The photoillumination was provided by four commercial blacklight-blue fluorescent

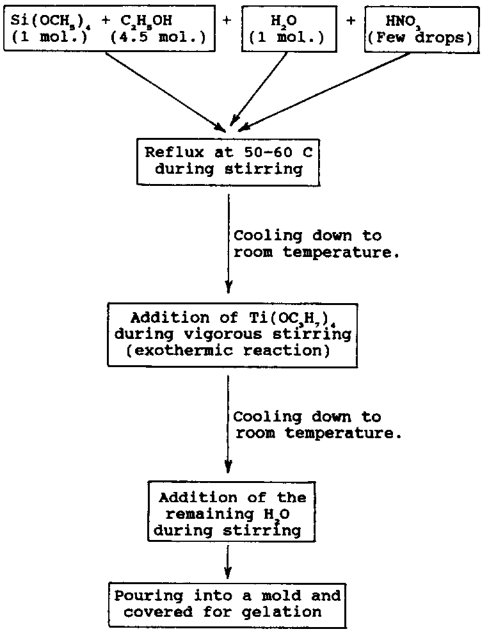

Fig. 1. Flowchart of the sol–gel procedure used to prepare TiO_2–SiO_2 alcogels.

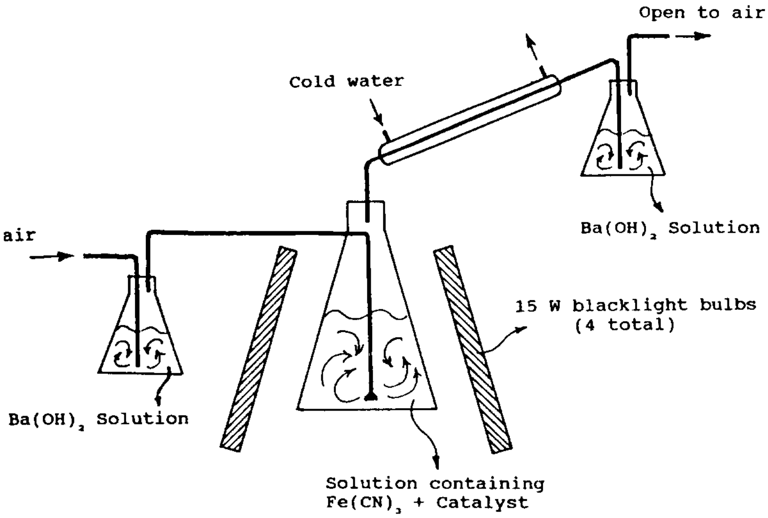

Fig. 2. Schematic diagram of photocatalytic reactor.

bulbs (GE BLB – 15 W), arranged parallel to the reactor sides, as shown in Fig. 2.

Control tests with irradiated solution in the absence of photocatalyst or photocatalyst containing solution in the absence of irradiation were carried out.

Periodically, about 10 ml sample of the reacting solution was withdrawn by a syringe and analyzed for concentration of ferric cyanide, using a spectrophotometer. The outlet gas stream from the reactor was passed through dilute barium hydroxide solution for determination of CO_2.

After the photocatalyzation process, the photocatalyst was filtered out, washed with distilled, deionized water, dried and weighed. Then, the photocatalyst recovery was calculated by applying the following relation:

$$\text{Recovery\%} = (W/W_0)\ 100,$$

where W_0 is the weight of the catalyst before the photocatalyzation process and W is the weight of the photocatalyst collected after the process.

To check for the activity loss of the aerogel catalyst, a series of runs was carried out by mixing a dilute solution (522 ppm) of ferric cyanide with the aerogel ($TiO_2:SiO_2$ molar ratio = 1 : 3.9), under the same experimental conditions as before. At the end of the run, the reactor was rinsed and the aerogel was filtered out, washed with distilled, deionized water, and re-used in subsequent runs. This procedure was repeated three times under the same conditions.

3. Results

Dark, opaque and cracked monolithic TiO_2–SiO_2 aerogels were obtained after supercritical drying of the corresponding alcogels. Heat treatment converted the aerogels to a white and translucent appearance. This was due to elimination of organic residues [14]. Fig. 3 shows a photograph of two monolithic aero-

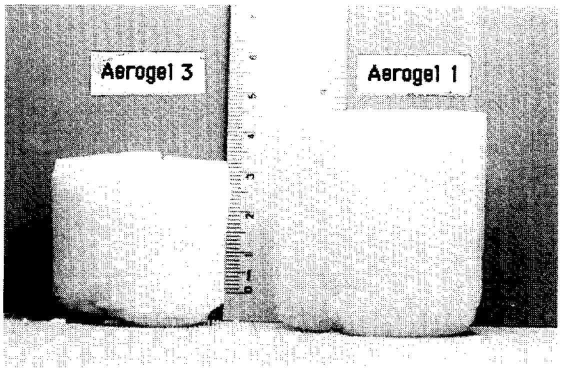

Fig. 3. Two monolithic aerogels after heat treatment; aerogel 1 with $TiO_2:SiO_2$ molar ratio = 1 : 3.9 and aerogel 3 with $TiO_2:SiO_2$ molar ratio = 1 : 1.3).

Table 2
Effect of $TiO_2:SiO_2$ ratio on shrinkage, density and appearance of TiO_2–SiO_2 aerogels

$TiO_2:SiO_2$ (molar ratio)	Shrinkage (%)		Apparent density (g/cm^3)	Appearance
	linear	volume		
1:3.9	25	59	0.27	translucent
1:2.6	35	67	0.39	translucent (< the above)
1:1.3	41	79	0.56	opaque

gels after heat treatment (aerogel 1 and aerogel 3 with $TiO_2:SiO_2$ molar ratios = 1:3.9 and 1:1.3, respectively) prepared from the same volumes of alcogels

Table 2 shows the effect of composition of the starting solution, i.e., $TiO_2:SiO_2$ molar ratio, on the shrinkage, apparent density and appearance of the produced aerogels. It was observed that, with decreasing SiO_2 content, the shrinkage and apparent density increased, but the translucency decreased.

Results obtained from the photocatalyzed oxidation of CN^- with the different forms of TiO_2 photocatalyst used in this study (Table 2) are illustrated in Fig. 4. These results have shown that in the presence of aerogel 1 ($TiO_2:SiO_2$ molar ratio = 1:3.9) about 43% of ferric cyanide was removed after 2 h illumination time, and after 6 h illumination time the removal reached about 94%. It is evident from this figure that, in the presence of the same amount of TiO_2 in the solution (i.e., 1 wt%), the photocatalytic activity of aerogel decreases with decreasing SiO_2 content. In addition, photocatalyzed oxidation of CN^- in the presence of anatase powder, with the same amount of TiO_2, appears to be equivalent to aerogel 2 and lower than aerogel 1. However, rutile powder had relatively very low activity for photocatalyzed oxidation of CN^- at the same conditions.

Results of control tests with irradiated solutions in the absence of photocatalyst, or photocatalyst (aerogel 1) containing solution in the absence of irradiation showed that no or very little oxidation of CN^- occurred under these conditions (Fig. 4).

In all experiments for photocatalyzed oxidation of CN^- in the presence of different forms of TiO_2 photocatalyst used in this study, a white precipitate was observed when the outlet gas stream was passed through the dilute barium hydroxide solution.

The estimated recoveries (%) of different forms of the tested TiO_2 photocatalysts, after the treatment process, showed the possibility of recovering approximately all the TiO_2–SiO_2 aerogels. However, it was difficult to recover all the TiO_2 powder used, e.g., about 16% of anatase powder and about 9% of rutile powder were contaminated with the effluent stream after filteration.

Results obtained from the series of runs to check for the activity loss of the aerogel photocatalyst are

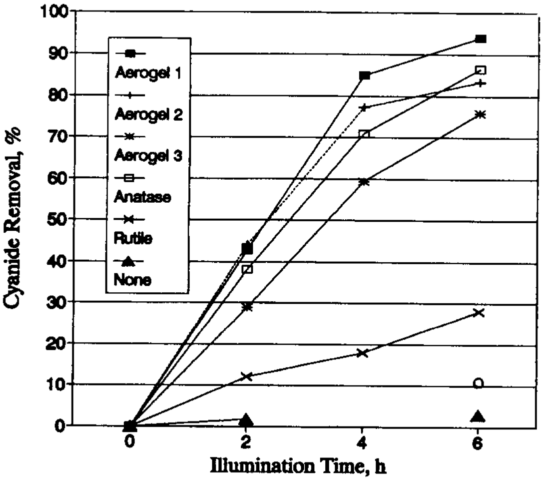

Fig. 4. Photocatalytic oxidation of CN^- in ferric cyanide solution (1000 ppm) using aerogels and particulate photocatalysts. (O, aerogel 1, but without illumination.)

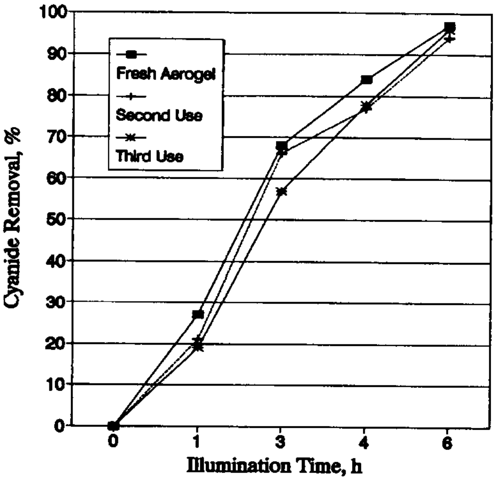

Fig. 5. Re-use of aerogel 1 in photocatalytic oxidation of CN^- in ferric cyanide solution (522 ppm).

illustrated in Fig. 5. No significant change in the aerogel photocatalyts activity was observed.

4. Discussion

The observed increase in shrinkage and apparent density by decreasing the SiO_2 content is due to the coalescence of gel particles which decrease the porosity, surface area and translucency [9,10]. However, decreasing shrinkage and apparent density, as well as increasing translucency with increasing SiO_2 content, can be explained by the fact that an extremely porous and transparent silica aerogel with a surface area of about 1600 m^2/g, can be produced by supercritical drying. However, titania aerogel (in the form of anatase) can exhibit a surface area of about 120 m^2/g [9]. So, increasing the SiO_2 content in the TiO_2–SiO_2 aerogel could have a positive effect on the porosity, surface area and translucency in the aerogel produced.

The increased photocatalytic activity of the aerogel with increasing SiO_2 content can be attributed to decreased shrinkage and increased surface area, as well as increased translucency.

The higher efficiency of anatase powder (as a photocatalyst) than rutile form was in part explained by possible trapping of electrons in the anatase form at the surface where they can more easily react with oxygen [4]. In addition, the higher particle size, i.e., lower surface area, of rutile powder in comparison with anatase powder, had a negative effect on photocatalytic activity.

In general, TiO_2–SiO_2 aerogels are expected to achieve superior performance to TiO_2 powder and colloid due to:

(a) increased surface area and porosity leading to improved reacton kinetics and extent;

(b) increased translucency due to presence of silica (titania particles are opaque) leading to improved utilization of light energy; and

(c) minimized loss of catalyst as aerogel granules and monolithic are easier to handle and recover for re-use than powders or colloids.

5. Conclusions

(1) Increasing SiO_2 content in the TiO_2–SiO_2 alcogel results in aerogel matrices with lower shrinkage (i.e., lower apparent density and higher surface area) and higher translucency. This leads to higher activity in the photocatalyzed oxidation of CN^- species.

(2) TiO_2–SiO_2 aerogel with higher SiO_2 content (i.e., TiO_2:SiO_2 molar ratio = 1 : 3.9) has higher efficiency than TiO_2 powder (i.e., anatase with $TiO_2 >$ 98%) in the photocatalyzed oxidation of CN^- species, when used with the same amount of TiO_2.

(3) One of the main advantages of using TiO_2–SiO_2 aerogel, as a photocatalyst for oxidation of CN^- species, is the possibility of recovering all the aerogel used after the treatment process for recycling. However, with using TiO_2 powder, it is difficult to recover all the powder used, e.g., about 16% of the used anatase powder was contaminated with the effluent stream after filtration.

(4) The aerogel photocatalyst can be re-used effectively several times without significant activity loss.

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