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Sol–gel synthesis of titania–silica photocatalyst for cyanide photodegradation

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Abstract

The results of a laboratory-scale study of an environmentally friendly water treatment method are presented, where the cyanide was removed by photocatalytic process. TiO_2–SiO_2 aerogel as photocatalyst has been prepared via sol–gel technique. Several factors were studied in order to find the conditions that could be used to synthesize this photocatalyst for optimum degradation of the cyanide pollutant in aqueous solutions. Best degradation was obtained by TiO_2–SiO_2 aerogel prepared by using a molar ratio of Ti:Si equivalent to 6:1. In addition, the molar ratios of other reactants such as $TEOS:H_2O:C_2H_5OH:HNO_3$ were taken as 1:8:10:0.25. These chemicals were reacted for 90 min at 25 °C. The produced gel was supercritical dried at 105 bar and 295 °C. Under the best conditions, TiO_2–SiO_2 aerogel, of a specific surface area of 850 m^2/g, resulted in cyanide removal efficiency of 98.74%. Details of the synthesis procedure and results of the characterization studies of the produced gel are presented in this paper.

1. Introduction

Cyanide is used in the production of organic chemicals such as nitrile, nylon, and acrylic plastics. Other industrial applications of cyanide include electroplating, metal processing, steel hardening, photographic applications, and synthetic rubber production. Gold mining operations use dilute solutions of sodium cyanide (100–500 ppm). Sodium cyanide is highly soluble in water and under mildly oxidizing conditions dissolves the gold contained in the ore. The chemical methods typically involve oxidation of cyanide by reagents such as SO_2–air, chlorine, permanganate, hydrogen peroxide, air and/or ozone. Photocatalytic oxidation over metal oxides, mainly TiO_2, has also been proposed as a possible option for cyanide elimination [1,2]. The use of TiO_2 as a photocatalyst for destruction of organic pollutants in aqueous waste streams has been studied extensively. Light absorption in TiO_2 at $\lambda < 385$ nm can be pumped with inexpensive UV lamp which effects the promotion of an electron from valence band to the conduction band of the semiconductor. This excitation process creates an electronic charge carrier in the conduction band and an electron vacancy (a hole) in the valence band [3]. Because the valence band edge of TiO_2 occurs approximately at 3.2 eV; the hole is very powerful oxidizing agent and is capable of oxidizing a variety of organic molecules as well as generating hydroxyl radical in water [4,5]. The use of TiO_2 anatase powder and other TiO_2 containing materials, for photocatalytic degradation of organic and inorganic pollutants has been studied extensively. Examples of such studies may include degradation of cyanide, glucose, propanol, chlorophenol, lignin and chain hydrocarbons using TiO_2 powder, TiO_2–SiO_2 aerogel [6–11]. Ismail et al. investigated photocatalytic oxidation of cyanide in presence of V_2O_5–SiO_2 xerogel [12] and TiO_2–SiO_2 xerogel and aerogel [13,14]. In the present paper, the authors have interested in preparation and optimization of TiO_2–SiO_2 aerogel as a photocatalyst to remove free cyanide compounds. Interestingly, the cyanide compounds have been broken down to N_2 and CO_2, which are environmental friendly. No attempts, however, were made to study the optimum conditions for preparation of TiO_2–SiO_2 aerogel as photocatalyst for degradation of CN^-, which is the subject of this investigation.

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2. Experimental materials

All chemicals used in this study were analytical grade reagents; the following high purity raw materials were used for TiO_2–SiO_2 preparation: titanium(IV) isopropoxide (TIIP) 97% Ti $[OCH(CH_3)_2]_4$; tetraethyl orthosilicate (TEOS) 98% Si $[OC_2H_5]_4$ Aldrich Chemical Co. and potassium cyanide from fisher.

2.1. Aerogel synthesis

TEOS was added to ethyl alcohol (EtOH:TEOS) and (1 mol H_2O:TEOS) and HNO_3 (1 M) as catalyst. The solution was magnetically stirred at various temperatures under inert gas in dry glove box. Then calculated amounts of TIIP with the retained water under vigorously stirring were added to complete the reaction then forming the sol. Soon after, the preparation beaker was covered with a plastic film to prevent chemical/solvent evaporation. The gelation time (t_g) was measured from the amount of water addition until the gel lost its fluidity. Drying of the TiO_2–SiO_2 gel was carried out under supercritical conditions at 243 °C and 63.6 bar (For Pascal (Pa) conversion multiply by 100000) using ethyl alcohol [10]. For this reason, the gel was 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 twice with 2 bar dry N_2 and finally pre-pressurized up to 10 bar N_2. The temperature of the autoclave was increased, at a heating rate of 2 °C/min, to a temperature of about 294 °C. The pressure in the autoclave increased to about 105 bar. After stabilizing the maximum temperature and pressure for 2 h, the vapor outlet micro-metering valve of the autoclave was slowly opened to vent out the solvent to the condenser. All the solvents from the autoclave was evacuated in 2–3 h at a constant temperature of about 294 °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 were 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. Then the TiO_2–SiO_2 aerogel samples were heat treated at 550 °C for 5 h.

2.2. Photocatalytic evaluation

All the experiments were carried out by using a horizontal cylinder annular batch reactor. A black light-blue florescent bulb (F18W-BLB) was positioned at the axis of the reactor to supply UV illumination. The light intensity after passing through a reaction suspension was 365 nm. The experiments were performed by suspending 2 g of TiO_2–SiO_2 aerogel into the reactor with 300 ml potassium cyanide (100 ppm). Cyanide was selected, as a model for the photocatalytic degradation experiments because it is nonvolatile and is a common contaminant in the industrial wastewaters. The re-

action was carried out isothermally at 25 °C and pH of 8–10 to avoid evolution of the toxic HCN gas and samples of the reaction mixture were taken every 1.0 h for a total reaction time of 6 h. The CN^- content in the solution after reaction time was analyzed by volumetric titration with $AgNO_3$ [15]. The removal efficiency of CN^- was estimated by applying the following equation:

$$removal\ efficiency\ (\%) = \left(\frac{C_o\text{-}C}{C_o}\right) \times 100$$

where C_o is the original cyanide content and C is the residual cyanide in solution.

2.3. Characterization of arogel samples

The surface area of the samples was measured by nitrogen physisioption using micro-meritics surface area analyzer. X-ray diffraction analysis (XRD) was carried out using Philips X-ray diffractometer (type PW 1730). Infrared spectra were measured in potassium bromide with fourier transform and pye-unicam SP 300 instruments.

3. Results and discussion

3.1. Effect of Si/Ti molar ratio

Influence of Si/Ti molar ratio on cyanide removal efficiency and surface area was studied under the following conditions $TEOS:H_2O:C_2H_5OH:HNO_3$ as molar ratios were 1:4:5:0.25 and reaction time of 90 min at reaction temperature of 25 °C. We found that Si/Ti molar ratio changed from 1:1 to 10:1 the gelation time increased from 50 min to 30 h. This attributed to the decrease in the percentage of Ti. This may be interpreted on the basis of the fact that titanium is transition metal has very electropositive charge. Values of $\delta(M)$ calculated from the partial charge model $\delta(M)$ of $Ti(OEt)_4$ and $Si(OEt)_4$ are +0.63 and +0.32, respectively [19]. Thus, titanium has duplex silicon of electropositive charge, which explains why the hydrolysis and condensation kinetics of titanium alkoxide is much faster than that of $Si(OEt)_4$. In this regard, literature values of the hydrolysis rate for $Si(OEt)_4$ range 10^{-4} to $10^{-6}\ M^{-1}\ S^{-1}$, whereas $Ti(Opr)_4$ is $10^{-3}\ M^{-1}\ S^{-1}$. In other words, hydrolysis of $Ti(Opri)_4$ is more 10–100 times than $Si(OEt)_4$. In addition, it was observed no gel was formed, but only a white precipitate appeared at 1:1 Ti/Si molar ratio. This could be attributed to the percentage of TiO_2 was as high as 9.88% in solution, whereas this reaction requires the concentration in solution not to exceed 5% TiO_2. Moreover, as Si/Ti molar ratio changed from 1:1 to 10:1 the surface area increased from 514 to 710 m^2/g as shown in Fig. 1. Thus, the increase in concentration of Si increases the specific surface area. This is due to contribution from the high surface area of SiO_2 aerogel (1600 m^2/g) as compared to 120 m^2/g for TiO_2 aerogel. The X-ray diffraction analysis for three samples Si/Ti ratio
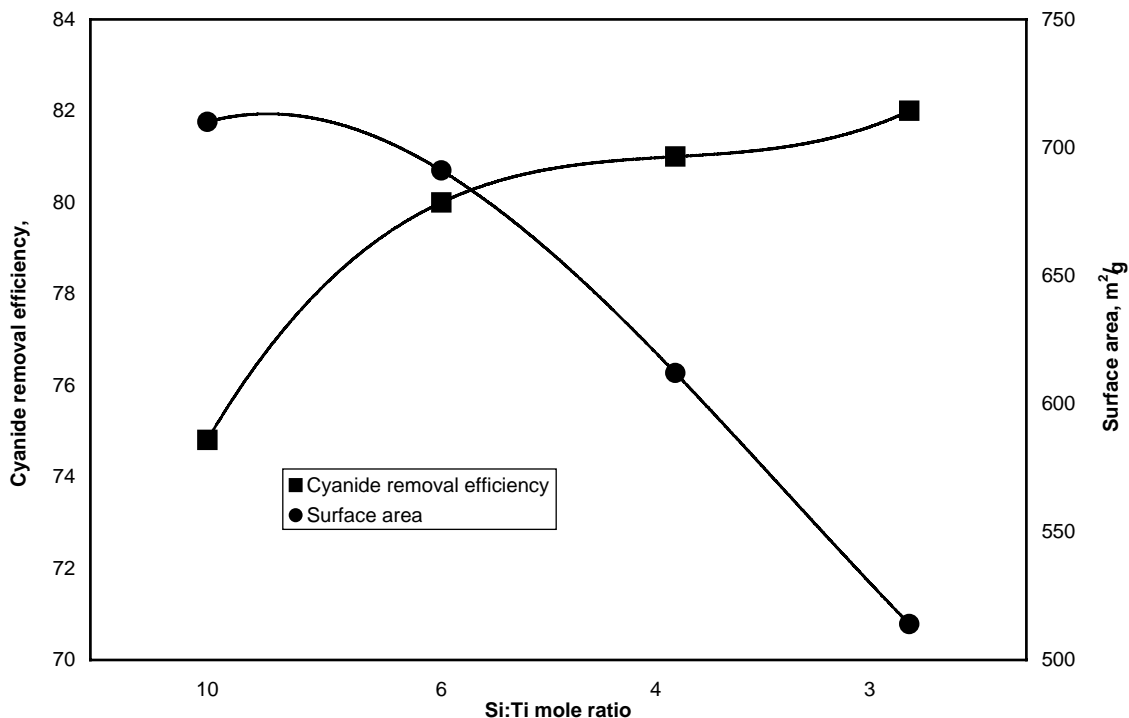
Fig. 1. Influence of Si:Ti molar ratio on surface area and photoactivity.

3:1, 4:1 and 6:1 has been performed as shown in Fig. 2. The results indicate that TiO_2 is found as anatase whereas SiO_2 was formed as amorphous phase. Also, the peak intensity is high and sharp at high percent of TiO_2 content. The results shown in Fig. 1 suggest that as Si/Ti molar ratio changed from 3:1 to 10:1 the CN^- removal efficiency decreased from 82.0 to 74.8%, which means that as the amount of Ti is reduced the removal efficiency decreases even though the surface area is increased. It should be mentioned here that the effective material for photocatalytic degradation is TiO_2 not the SiO_2.

3.2. Effect of C_2H_5OH/TEOS molar ratio

Effect of C_2H_5OH/TEOS molar ratio on cyanide removal efficiency, gelalion time and surface area is shown in the Fig. 3. The data illustrates that as the C_2H_5OH/TEOS molar ratio increases from 2 to 15 the surface area of the sample
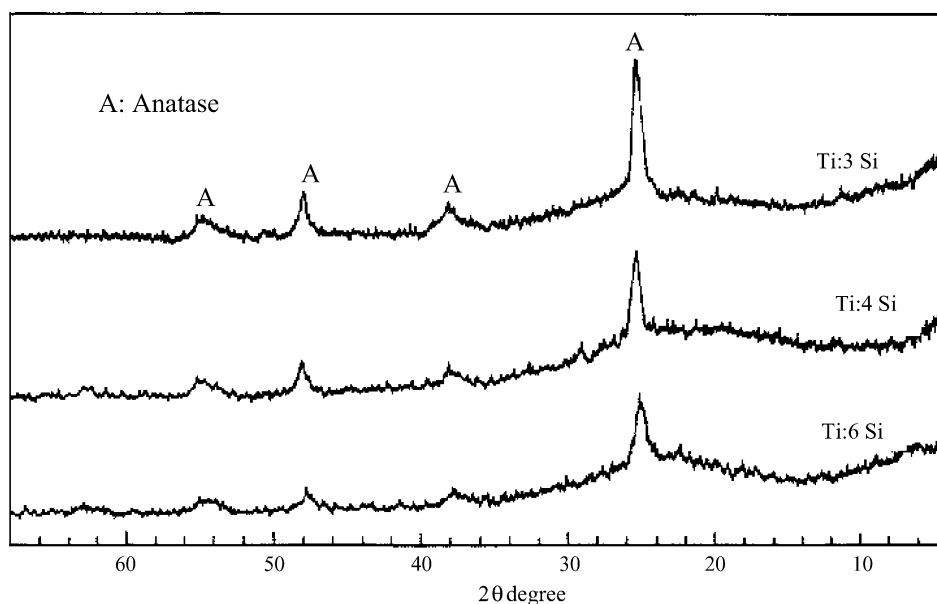
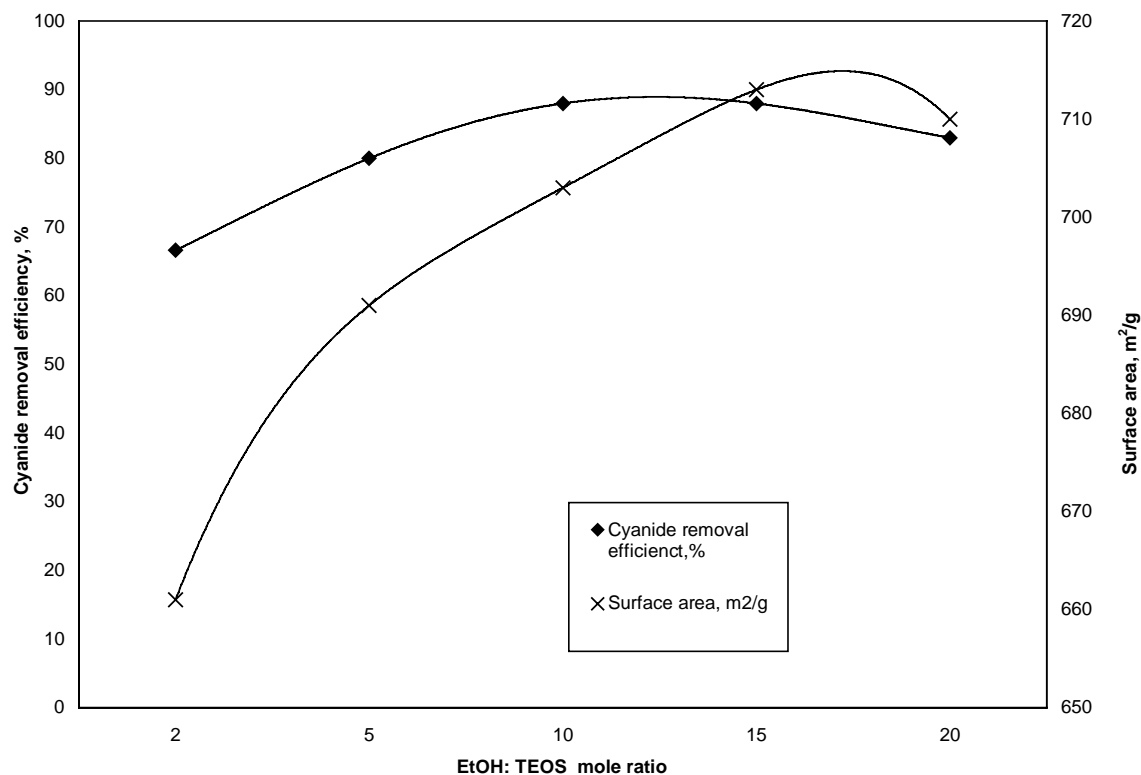

Fig. 2. XRD of titania–silica at different composition.

Fig. 3. Influence of EtOH:TEOS molar ratio on surface area and cyanide removal efficiency.

is increased from 661 to 710 m^2/g. Most importantly, CN$^-$ removal efficiency is increased from 66.1 to 88.0% corresponding to such increase in the C$_2$H$_5$OH/TEOS molar ratio. It is interesting to note in the same figure, the decrease in removal efficiency (at higher TEOS content), without significant decrease in surface area. This could be attributed to a decrease in solution viscosity at high TEOS content. Thus, the polymerization of sol to alcogel requires further time to complete the polycondensation reaction. In addition, one may speculate that alcoholysis of siloxane bonds (reverse) provide means for bond breakage and reformation allowing continual restructuring of the growing polymer [19]. Consequently, during the supercritical drying and heat treatment, the sample has collapsed and became opaque so that cyanide removal efficiency was decreased by increasing the C$_2$H$_5$OH/TEOS molar ratio. Based on these results, the optimum conditions of C$_2$H$_5$OH/TEOS molar ratio is considered 1:10 at 34 h gelation time, leading to 88.0% cyanide removal efficiency.

3.3. Effect of H$_2$O:TEOS molar ratio

The hydrolysis reaction was performed at H$_2$O:TEOS molar ratio (r) ranging from 4 to 20. The results are given in Fig. 4. It can be seen that low values of r generally promote hydrolysis. When r is increased, while maintaining a constant solvent: TEOS ratio; TEOS and TIIP concentrations are reduced. Consequently, the hydrolysis and conden-

sation rates are reduced, causing an increase in the gel time. Moreover, when r increases from 4 to 8 the specific surface area increases from 703 to 766 m^2/g. At higher values of r (r is changed from 12 to 20), however, the specific surface area is decreased to 433.8 m^2/g. The reason suggested for this behavior is that acid-catalyzed low-water solutions produce linear polymers and higher-water solutions produce cross-linked polymers or branched-clusters [16–18].

In addition, a series of experiments has been carried out to study photoactivity of the samples at different r values and under aforementioned conditions. The results presented in Fig. 4 reveal that when the r values increases in the range of 4 to 20, the CN$^-$ removal efficiency increases from 88.7 to 99.8% at $r = 8$ then the removal efficiency decreases from 99.80 to 89% with increasing the r values from 8 to 20. This may be attributed to the transparency of the sample to light. For example, at low water content, the produced samples were observed to be more translucent. At large values of H$_2$O:TEOS molar ratio (r) siloxane bond hydrolysis tends to the reverse reaction. The hydrolysis reaction may proceed in the reverse direction, in which an alcohol molecule displaces a hydroxyl group to produce an alkoxide *ligand + water* as by-product. This reverse process occurs via the mechanism of bimolecular nucleophilic substitution reaction as reported in [19]. This renders the produced samples at high water content to be opaque. The optimum condition of H$_2$O/TEOS molar ratio may be considered as 8:1 giving 99.8% cyanide removal efficiency.
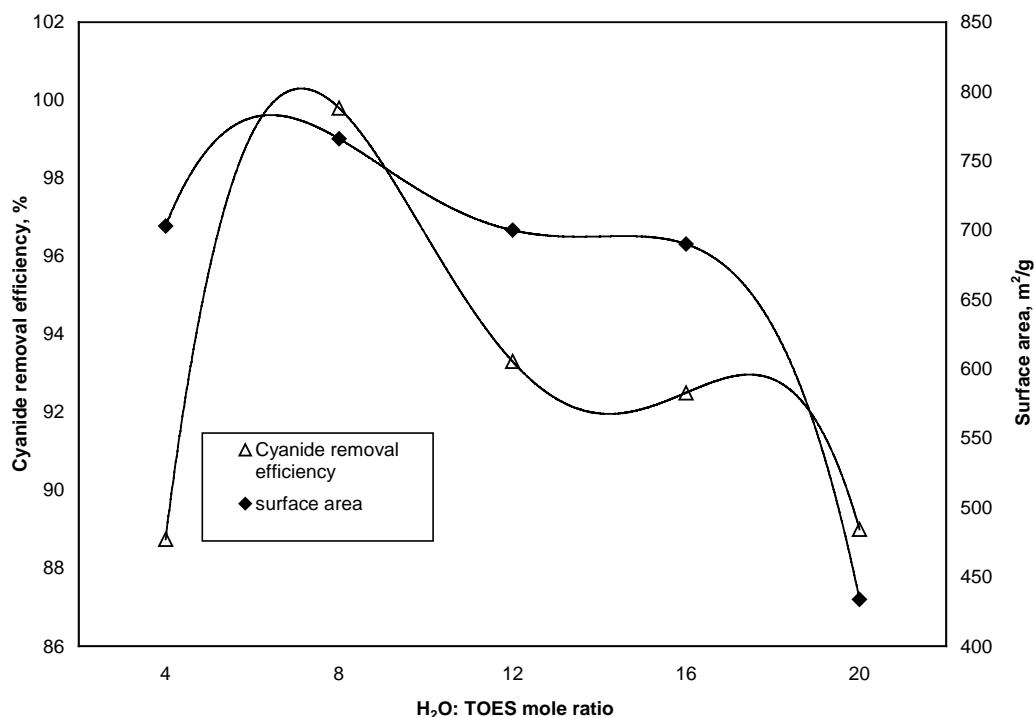
Fig. 4. Influence of H2O:TOES molar ratio on surface area and photoactivity.

3.4. Effect of acid catalyst

Under acidic conditions, it is likely that an ethoxide group is protonated rapidly as a first step. Electron density is withdrawn from silicon, making it more electrophilic and thus, more susceptible to attack by water [19]. The results summarized in Table 1 shows that when HNO_3:$Si(OC_2H_5)_4$ molar ratio increases from 0.035 to 0.25 the hydrolysis and condensation rates increase thus, the gelation time decreases from 39 to 12 h. However, it is noticed that as HNO_3:$Si(OC_2H_5)_4$ molar ratio increases above 0.25 the gelation time increases to reach 28 h at 0.355 HNO_3:$Si(OC_2H_5)_4$ molar ratio. This has been interpreted on the basis of the extent of hydrolysis and polymerization [19]. The hydrolysis rate is increased by substituents that reduce steric crowding around silicon. In addition, titanium electron-providing substituent that helps stabilize the developing positive charge, should also increase the hydrolysis rate. At higher acid volume, an increase of the

gelation time may be attributed to the amount of acid catalyst increases in solution, making disturbance in the transition state and hence silanol with TTIP. It is known that the hydrolysis mechanism is sensitive to inductive effects (based on the consistent trends) and is apparently unaffected by extent of alkyl substitution. Thus, increase in stability of the transition state will increase the reaction rate [19].

3.5. Effect of reaction temperature

The results given in Table 2 shows that as the reaction temperature increases from 25 to 62 °C the gelation time increases from 12 to 76 h. This can be attributed to the substitutes of alkyl group that increases steric crowding in the transition state, would retard condensation at high temperatures. In other words, the solvent might have lost the ability to form hydrogen bonding and hence condensation rate decreased [20]. Moreover, the CN^- removal efficiency decreased from about 98.7 to 85.2%. Therefore, the optimum condition of reaction temperature is considered

Table 1
Effect of acid catalysis on photodegradation of cyanide ions

HNO_3 (1 M):$Si(OC_2H_5)_4$ molar ratio	Gelation time (h)	Surface area (m^2/g)	CN^- removal efficiency (%)
0.035	39	735.6	87.0
0.106	36	766.0	99.8
0.177	19	783.0	97.3
0.25	12	850.0	98.7
0.355	28	834.8	92.0

Table 2
Effect of reaction temperature on photodegradation of cyanide ions

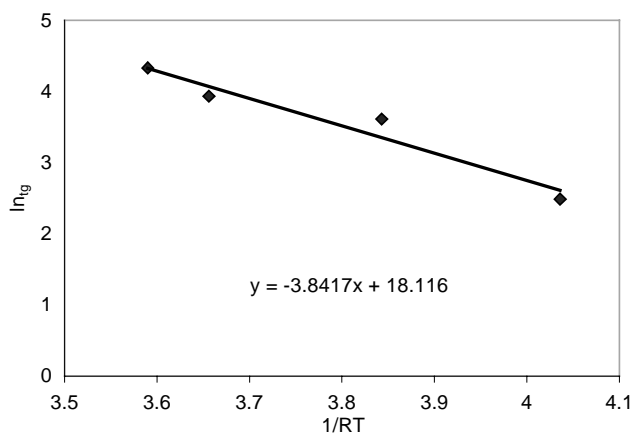| Reaction temperature (°C)	Gelation time (h)	CN^- removal efficiency (%)
25	12	98.7
40	37	88.6
56	51	86.6
62	76	85.2

Fig. 5. Effect of temperature on gelation time.

25 °C, at which 98.7% removal efficiency of cyanide can be achieved.

The apparent activation energy has been determined by the following Arrhenius equation [21]:

$$\frac{1}{t_g} = A \exp\left(-\frac{E^*}{RT}\right)$$

where t_g is gelation time, A the Arrhenius constant and E^* is the activation energy.
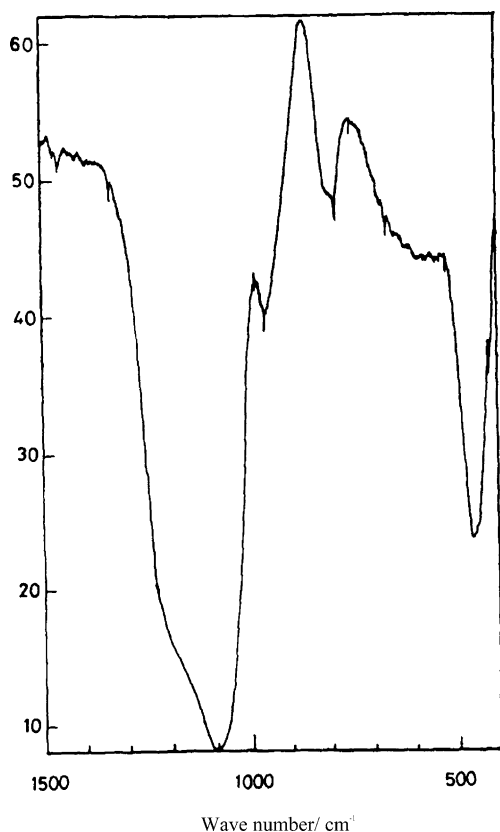

Fig. 6. IR spectra of TiO$_2$–SiO$_2$.

The data are plotted to give a linear relationship between $\ln t_g$ and $1/RT$ as shown in Fig. 5. The apparent activation energy is calculated from the slope of the line. The intercept is the Arrhenius constant (A). The activation energy is estimated to be -2.692 cal g^{-1} mol (For Joule (J) conversion multiply by 4.187) and A is 1.26×10^{-6} h^{-1}.

3.6. Characterization of optimized TiO$_2$–SiO$_2$ aerogel

The IR spectra of the TiO$_2$–SiO$_2$ aerogels, calcined in air at 550 °C are shown in Fig. 6. The homogeneity is evaluated by the peak intensity of the Ti–O–Si band that is observed sharply at 960 cm^{-1}, assigned to ν(Ti–O–Si) vibrations. However, another band appears at 1030 cm^{-1} that is assigned to ν(Si–O) vibrations. These findings are in agreement with previous studies [22–25]. In addition, TiO$_2$–SiO$_2$ sample was examined using SEM and electron probe for chemical analysis. Chemical composition of this particles was determined to consist of 85.78 at.% Si and 14.22 at.% Ti. It may be concluded that the binary TiO$_2$–SiO$_2$ xerogel has a homogeneous matrix.

4. Conclusions

The TiO$_2$–SiO$_2$ mixed oxides has been prepared via sol–gel approach using TEOS and TIIP. The conditions that could be used to obtain aerogel material that can be used efficiently for photocatalytic degradation of cyanide may be listed as:

- Si:Ti: molar ratio of 1:6;
- C$_2$H$_5$OH:TEOS molar ratio of 10;
- H$_2$O:TEOS molar ratio of 8;
- HNO$_3$ (1 M):Si (OC$_2$H$_5$)$_4$ molar ratio is 0.25.

The optimized sample has been used as photocatalyst for degradation of cyanide and the removal efficiency of cyanide is 98.7% at 850 m^2/g specific surface area.

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